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Physics. — *Separation of substances by flotation.* II. By F. K. TH. VAN ITERSON.

(Communicated at the meeting of February 27, 1937).

3. *Some physical facts about surface tension.*

In clean water there is no orientation of the molecules near the surface. The molecules at the surface are attracted inwards and to each side by their neighbours, but there is no outward attraction to balance the inward pull.

Hence every surface molecule is subject to a strong inward attraction perpendicular to the surface.

Our country-man DEBYE has given an explanation for this attraction [1]) which with a slight modification is now generally accepted. This is only mentioned to emphasize the fact that there is no "contractile skin" or physical tension parallel to the surface of liquids. The hypothesis of surface tension is introduced because this substitution gives the same mathematical free energy per unit area and all the calculations based thereon are exact.

We now calculate the surface-energy liberated when an air bubble sets on a flat surface of a piece of coal under water.

In figure 9 the contents of pending and fixed air bubble are the same.

Hence $\frac{4}{3}\pi r_0^3 = \frac{9}{8}\pi r^3 \qquad r = 1{,}0584\, r_0$.

In order to simplify calculations we only figure with the difference in tension of the surface of separation between liquid and solid and that between solid and air because these two vectors are always in line and only their difference counts. We call this difference γ_s. With the angle of contact $\vartheta = 60°$

$$\gamma_s = -\tfrac{1}{2}\gamma_{gl}\,.$$

When the bubble sets on the coal the spherical surface diminishes from $4\pi r_0^2$ to $\frac{3}{4} \times 4\pi (1{,}0584\, r_0)^2$ or $0{,}16 \times 4\pi r_0^2$.

The coal surface which becomes dry $= \frac{3}{4}\pi(1{,}0584 r_0)^2 = 0{,}84\,\pi r_0^2$.

The total energy set free when the bubble sets on the coal is

$$0{,}64\pi r_0^2 \gamma_{gl} - 0{,}84\pi r_0^2 \gamma_s = (0{,}64 - 0{,}42)\pi r_0^2 \gamma_{gl}\,.$$

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[1]) Die VAN DER WAALSschen Kohäsionskräfte von P. DEBYE, Physik. Zeitschrift XXI, 1920, p. 179.

This being positive energy a bubble has the tendency to fix itself to a coal surface; or air coming free from the water in which it was dissolved, by

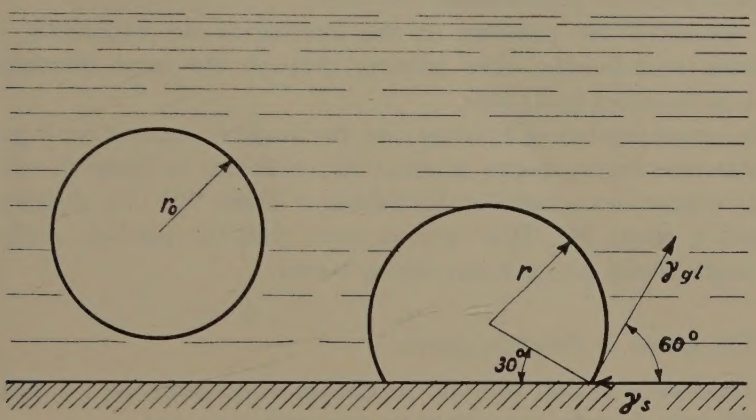


Fig. 9. An air bubble sets on a piece of coal with an angle of contact $\vartheta = 60°$.

preference does so on a water repelling surface. As two bubbles by combining contract their surface, larger bubbles will grow at the expense of the smaller ones, until they rise to the surface.

It is clear now, that the technicians dispose of three methods of bringing floatable minerals to the surface.

1. Pressure flotation. Air is dissolved in water and the pressure released.
2. Vacuum flotation. Water saturated with air under atmospheric pressure is brought under vacuum.
3. Pneumatic flotation. Finely divided air is blown through the agitated pulp.

We never float substances with clean water. Chemical reagents or at any rate organic substances, containing hydro-carbons, are added to the water. And since the molecules are free to move, the liquid will always tend to cover itself, at the surface, with the molecules of the constituent which gives the smallest free surface energy. The concentration of solved substances at the surface differs from the concentration in the bulk of the liquid because generally the watermolecules attract each other with a greater force than the molecules of those organic substances. So these are pressed to the surface. It takes some time before these surfaces are built up. We later on must mention their polar constitution and the difficulty which large molecules have in orientation. These phenomena account for the lag in time and shape of expanding and contracting bubbles.

In figures 10 and 11 these phenomena are represented. Expansion is obtained when the cold water takes the temperature of the laboratory, contraction by adding ice.

The difference in angle of contact of an expanding and a contracting air bubble is called hysteresis. And as the polar molecules, orientated in

the surface, really interact by electro-magnetic forces, this expression, which is taken from the similar behaviour of magnetized and demagnetized iron, gives a correct representation of facts.

We measured the pressure in the interior of an expanding and a contracting soap-bubble when passing through the same diameter and found a pronounced hysteresis.

In the actual practice of floating coal, the angle of contact for a growing air bubble (the drying angle) is about 60° as shown in figure 6, while the angle of contact for a contracting bubble is about 90°, the difference or hysteresis is about 30°. We have to count with the smallest angle. The larger angle would give a better lifting power.

4. *The action of flotation agents.*

It is impossible to deal with all the classes of reagents used in flotation. We shall only describe some of their principal functions.

I. *Collectors.*

Collecting agents are oily substances. They are immiscible in bulk with water, but when mixed in the proportion usual in flotation operations, viz.: 1 : 4000 to 1 : 80.000 all of them dissolve to some extent. If applied under water in high concentration they ought to show a tendency to wet, to spread over the material that must be floated, but not displace the water from the surface of the material, which must sink.

Metals, coal, sulphides are easily coated with these fatty substances and repel the water, causing a preferential precipitation of gas from super-saturated solutions of gas.

The adsorbtion of these so-called collectors from their solution in water is physico-chemical in nature and belongs to the colloid-chemistry.

For practical application we mention some facts, which at the same time throw some light on the physico-chemical action of these reagents.

1°. The amount of collecting agents to be adsorbed in order to effect a satisfactory recovery of most materials is that needed for the formation of a mono-molecular film or less. Under water these substances show a preference to be adsorbed by the more floatable substance.

2°. All the collecting agents which serve to give our material a fatty surface are organic substances, containing one or more aliphatic groups ($—C_n H_{2n+1}$). The larger this group is, the better, because the angle of contact increases with the length of the adsorbed molecule.

3°. Crystals and apparent amorphous substances, which have a crystalline nature, have free attractive forces. The powerful flotation reagents, xanthates, aerofloat and the like, fix themselves polarly orientated on the crystals, the group with S combines with the substance to be floated, the aliphatic groups are directed outward and the skin shows a water repellent nature.

a *b* *c*

Fig. 10. *a*. expanding air-bubble under water on a polished coal-surface, wetted with tar-oil.
b. the same air bubble contracting.
c. the same bubble in a more advanced stage.
Magnification 40-fold.

a *b* *c*

Fig. 11. *a*, *b* and *c* different stages of a contracting bubble when more tar-oil had been added.
Magnification 40-fold.

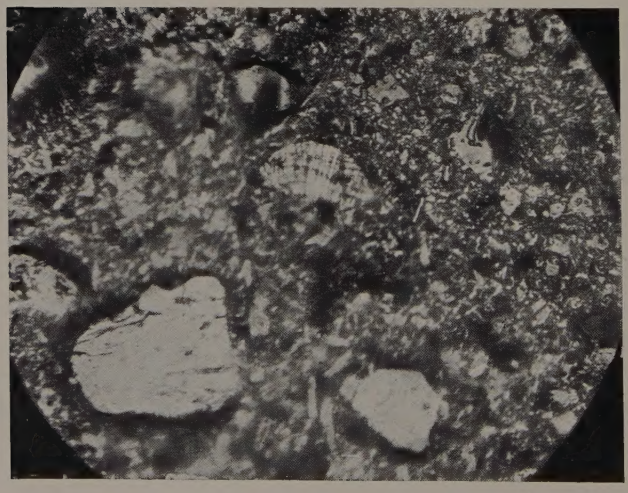
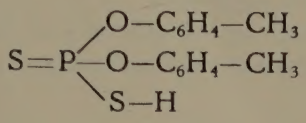


Fig. 12. Photograph of an air-bubble loaded with coalparticles, magnification 270-fold.

With such chemicals it is possible to float phosphates and carbonates of *Ca, Mg, Fe, Mn,* etc. aerofloat = dicresyldithiophosphoric acid



For floating coal petroleum products are often added.

The manufacture of flotation agents is one of the flourishing chemical industries in the United States.

II. *Frothing agents.*

It would be impracticable to float materials with clean water. Try to float three needles. You will see that the depressions in the water surface unite. The contraction of the surface simulates attraction of the floating objects, they sink together.

In practice the area of a flat surface required to float a ton of mineral would be prohibitively large. The necessary surface is produced in the interior of the liquid by forming a froth of bubbles.

The bubbles float to the top, where the mineral accumulates as a scum and is swept off.

Reagents for the formation of froth must be added to the water.

Frothing agents are organic compounds consisting of a water-repellent and a water-avid group. In the bubbles the hydroxyl —*OH*, the carboxyl —*COOH*, the amine —NH_2 etc. by preference place themselves on the waterside, the hydrocarbon group, being water-repellent will be directed away from the water. Films of this nature may have a sufficient stability to carry the solid particles to the surface. Thereby the mineral particles themselves act to some extent, as froth stabilizing agents. The surface of the bubble cannot contract indefinitely if there are particles of powder in it. This contraction squeezes out much of the liquid.

Figure 12 gives a photograph of a part of an air bubble loaded with coal. All the particles are placed with their largest dimensions in the surface. No free space is left.

The best of all substances for producing froths, soaps, are useless in floating minerals. When tried for coal it is interesting to see that the coal-particles move into the liquid. The explanation is that the tension of the surface between air and water diminishes to such an extent, that the coal surface is completely wetted.

A glance at figure 9 will make clear what happens when $\gamma_{gl.}$ decreases below γ_s.

A simple experiment with soap-bubbles showed us that the surface tension is only 0,013 g/cm against 0,0722 of pure water. (For soap-water we found $\gamma_{gl} = 0{,}02$).

A condition for suitability as frothing agent is that the surface tension of the water ought not to be lowered too much. Phenol and cresolic acids ($CH_3C_6H_4OH$) meet this condition.

At the State Mines we use the effluents of the ammonia and benzole recovery plants of the coke-ovens containing these substances and some tar oil.

III. *Activators.*

These have a chemical action and modify the surface. For the flotation of ZnS some $CuSO_4$ is added to form a partial coat of CuS on the mineral, as CuS belongs to the substances which are most easily floated.

IV. *Depressing agents.*

These serve to prevent temporarily or permanently the flotation of the materials which are required to sink. The most usual depressant is $NaCN$ for instance added to ZnS, the cyan-ion forms with the Zn-ion the insoluble $Zn(CN)_2$ which is hydrophil (easily wettable). The water covers the mineral particles and prevents them from floating.

V. *Sulphidisers, promotors, conserving agents, pH regulators, dispersion agents.*

With the exception of the latter, whose apparent physical effect is causing flocculation of the pulp, these agents are chemical in action.

The science of flotation is so advanced, that this method of separation seems applicable for any mixture of solid materials.

As only a monomolecular layer or even less of the agents is needed to influence the angle of contact of the air-water surface, flotation is the most economical method of separation.

5. *The coal-slurry flotation plant of the State Mines in Limburg (Holland).*

The State Mines in Limburg operate the largest coal flotation plants in the world. The daily production of flotated coal, calculated as dry material is 1500 tons at mine Maurits, 900 tons at mine Emma and 700 tons at mine Hendrik. Since flotation was introduced in 1921 the State Mines work with profits, without flotation the exploitation of the State Mines would have resulted in heavy losses.

Dr. CHR. TH. GROOTHOFF, the present chief mining engineer of the State Mines, acquainted with this method of separating metal-sulphides from the gangue proposed and stimulated a thorough investigation of the applicability for the purification of the finest grade of our coal, the slurry of our coal washeries, containing about 20 % of ash, which hitherto was partly sold to local consumers and partly was rejected in the streams. The research work was done by our chief mechanical engineer

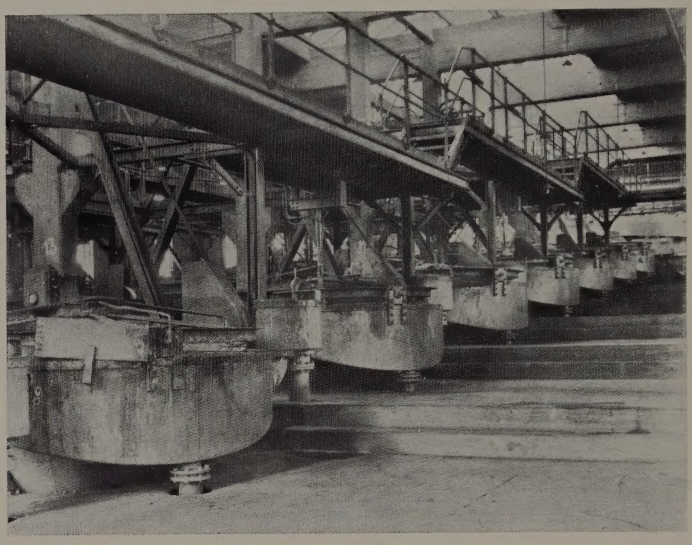


Fig. 14. Some flotation machines for coalslurry working in series at Mine Maurits.

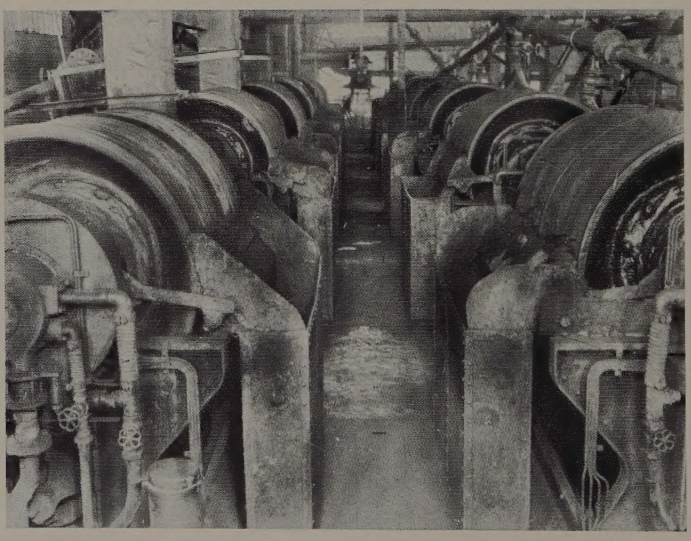


Fig. 15. Suction filters for dewatering flotated coal.

J. W. KLEINBENTINK, who in a short time developed the agitation froth machine, which bears his name. In this apparatus, represented in figure 13 the pulp of relatively high dilution (12 % of solid material) enters through the sloping influent pipe, with an ash content of about 20 %. Some tar oil, about ½ l. per ton of solid coal, is added to the slurry, which is also mixed with the effluents of the cokebyproducts factories, containing phenol and cresols. At Mine Maurits the water is sufficiently polluted with tar oil so that no collector is needed. The oils are for the greater part absorbed by the coal. (At the Champion Mine of the Pittsburgh Coal Company ½ lb cresolic acid is used as frothing agent and $^1/_8$ lb of fuel oil as collecting agent, calculated per ton of dry material.)

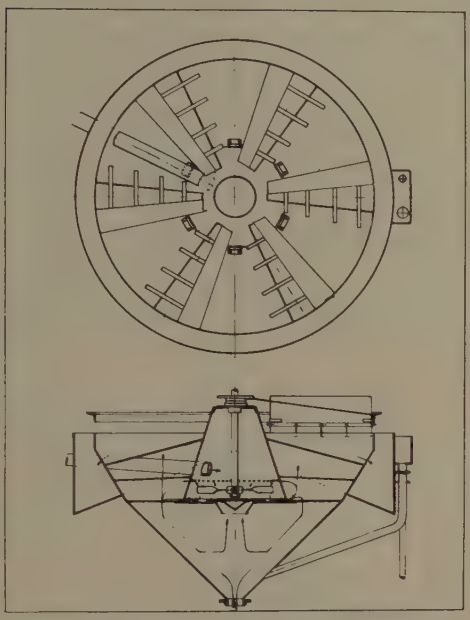


Fig. 13. KLEINBENTINK flotation machine.

The propellor in our machine, running 350 revolutions per minute, provokes a whirlpool in the inner cone. In the cavitation zone of the propellor-blades air is fixed to the coal particles. The pulp with the air bubbles passes through a ring-slot to a quieter space in the outer cone. The shale particles descend through the lower perforated plate and are partly evacuated. As indicated the slurry partly recirculates. The coal-carrying froth rises through the upper plate.

Six skimmers hanging on revolving arms push the froth into six radially placed gutters. In order to flotate with the smallest quantity of chemicals several apparatus work in series.

A view of a part of the flotation plant at Mine Maurits is given in figure 14.

The next figure 15 gives a picture of a set of suction filters placed on the floor below the flotation machines, which reduce the humidity of the flotated coal from 65 to 24 percent at Mine Maurits and from 65 to 21 percent at Mine Emma, where some boiled starch is added to the sludge.

The dewatered flotated coal is dried in a separate building in large gas-fired rotating drums before being mixed to the other coking coal.

The pulp entering the flotation machines contains 12 percent of solid matter.

The treatment of the tailings, a black liquid, containing about 3 percent of solid matter, shale particles and other dirt largely of colloidal fineness is a subject for a separate communication.

6. *Economical aspects of flotation.*

Any American library shows that by far the largest number of patents and other publications on ore-dressing bear on the separation of the minerals from their gangue by flotation. Last year more than 120 millions tons of material were flotated. With the exception of iron-ore which generally needs no concentration, 85 percent of the basicmetal-ores are subjected to froth-flotation. The cases in which flotation is successfully applied are rapidly increasing.

Especially gold ores are now concentrated by flotation and an enormous augmentation of the worlds gold production may be predicted for the next years. It is true, that flotation of the precious metals is only more efficient than either amalgamation and cyanidation if they are associated with sulphides.

The operation of the flotation plant is so much cheaper, the grinding may be so much coarser that even when sulphides must be mixed to the gold-ore, flotation generally lowers the cost of concentration. Next year the gold production of Russia and Canada, where the American flotation machines are in use, will probably surpass that of South Africa. But also in this continent the introduction of the new method will give the impetus to a modernization of the gold mining industry.

But not only metal ores, sulphur, graphite (diamond dust and bort are easily recuperated from dirt by flotation) and similar materials are recovered by flotation; in America every solid material which needs concentration passes the flotation machine. If the limestone of a cement-work contains too much quarz a part of the raw material is concentrated by flotation.

In Florida several phosphate mines earn more by flotating their refuse heaps than they formerly did by mining and dressing the rich phosphate pebbles.

Everybody, acquainted with the tables of VAN 'T HOFF for the separation of KCl from $NaCl$ by fractional leaching of sylvinite is now watching the rapid progress in the flotation of sylvite from halite in New Mexico.

The same collector, a thiol, can be used for floating away langbeinite ($K_2SO_4 2MgSO_4$) from halite.

Dr. H. A. J. PIETERS of the State Mines easily realised the separation of KNO_3 from NH_4Cl.

The contention that for technical separation of mixed solids flotation is always the most economical method seems justified by American practice.

This, however, holds true not only for the separation of one material from another. The Consolidated Mining and Smelting Co. of Canada Ltd., which did much pioneer work on flotation, which we visited in September 1936, are practising differential flotation on a large scale on a mineral whose principal constituents are galena marmatite, pyrrhotite and pyrite and separate this into lead concentrates, zinc concentrates and iron

concentrates. The drop in price of the base-metals is due for a large part to the American practice of flotation.

7. *Contribution of the State Mines in Limburg in the development of coal flotation.*

As already mentioned the State Mines were the first coal-mines which applied this process on an extensive scale. Numerous are the members of the staff and the workmen who contributed to the development. From our mines the application spread to Germany, Belgium and other countries and one private mine in Limburg followed our example. The difficulty which retards applications is the drying of the dewatered froth.

I am indebted to Dr. H. A. J. PIETERS, Dr. H. KOOPMANS and Ir. O. F. H. H. VAN DE LOO and other engineers for their assistance during the preparation of this communication.

Physics. — *Determination of the vapour pressures of liquid nitrogen below one atmosphere, and of solid nitrogen β. The boiling point and triple point of nitrogen.* By W. H. KEESOM and A. BIJL. (Abstract of Communication N°. 245*a* from the KAMERLINGH ONNES Laboratory of Leiden).

(Communicated at the meeting of February 27, 1937).

The vapour pressure curve of nitrogen has been determined between 53° K and 78° K (pressures between 0.8 cm and 78 cm).

From the vapour pressure of liquid nitrogen the temperature may be derived by the formula

$$\frac{1}{T+\triangle T} = -3.20398 \times 10^{-3} \,.\, {}^{10}log\, p + 1.89532 \times 10^{-2}$$

(p in cm Hg; T in °K; 0° C = 273.144° K on the Leiden scale).

The following list gives a number of values of $\triangle T$:

T	64	66	69	72	75	77
$\triangle T$	$+0.01_8$	0.04_6	0.06_8	0.06_7	0.04_3	0.00_9

From the measurements in the neighbourhood of the boiling point results for this temperature: $t_N = -195.78_7°$ C or $77.35_7°$ K.

For the vapour pressures of solid nitrogen β the following formula holds:

$$\frac{1}{T+\triangle T} = -2.7748 \times 10^{-3} \,.\, {}^{10}log\, p + 1.85350 \times 10^{-2},$$

if $\triangle T$ is taken by interpolation from the following list

T	54	57	60	63
$\triangle T$	$+0.00_2$	0.01_5	0.01_5	0.00_1

The triple point pressure has been determined by observing the constant

pressure at which liquid and solid nitrogen were coexistent. The triple point temperature was determined by interpolation on the vapour pressure curves for solid and liquid nitrogen. The result was:

$$P_{tr} = 9.401 \text{ cm}, \quad t_{tr} = -219.99_4 \,^{\circ}\text{C} \text{ or } 63.15_0 \,^{\circ}\text{K}$$

Within the experimental accuracy the vapour pressure data obtained are in accordance with caloric data.

Mathematics. — *Zur Differentialgeometrie der Gruppe der Berührungstransformationen. II. Normalform und Haupttheorem der doppelthomogenen Berührungstransformationen.* Von J. A. SCHOUTEN.

(Communicated at the meeting of February 27, 1937).

1. *Einleitung.*

In der ersten Arbeit [1]) wurde gezeigt, dass sich jede Berührungstransformation in den $2n-1$ Variablen $\xi^1, \ldots, \xi^n, \zeta_2, \ldots, \zeta_n$ nicht nur nach LIE als eine homogene Berührungstransformation in $2n$ Variablen $\xi^1, \ldots, \xi^n, \eta_1, \ldots, \eta_n$ schreiben lässt sondern auch als eine doppelthomogene Berührungstransformation in $2(n+1)$ Variablen $x^0, \ldots, x^n, p_0, \ldots, p_n$ die den Homogenitätsbedingungen (I. 25)

$$\left.\begin{aligned} x^\mu \partial_\mu x^{\varkappa'} &= x^{\varkappa'} \\ x^\mu \partial_\mu p_{\lambda'} &= 0 \\ p_\mu \partial^\mu x^{\varkappa'} &= 0 \\ p_\mu \partial^\mu p_{\lambda'} &= p_{\lambda'}, \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (1)$$

den Bedingungen (I. 28)

$$p_{\varrho'} x^{\varrho'} = p_\varrho x^\varrho \quad \ldots\ldots\ldots \quad (2)$$

und für $p_\varrho x^\varrho = 0$ auch den Bedingungen (I. 14, 16)

$$\left.\begin{aligned} p_{\varrho'} dx^{\varrho'} &= p_\varrho dx^\varrho \\ x^{\varrho'} dp_{\varrho'} &= x^\varrho dp_\varrho \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (3)$$

und den Bedingungen (I. 24)

$$\left.\begin{aligned} p_{\varrho'} \partial_\lambda x^{\varrho'} &= p_\lambda \\ x^{\varrho'} \partial_\lambda p_{\varrho'} &= 0 \\ p_{\varrho'} \partial^\varkappa x^{\varrho'} &= 0 \\ x^{\varrho'} \partial^\varkappa p_{\varrho'} &= x^\varkappa \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4)$$

(welche nur für $p_\varrho x^\varrho = 0$ *nicht* aus (3) folgen) genügt. Wir werden jetzt zeigen, dass wir die also erhaltene doppelthomogene Berührungstransformation stets, *ohne* die Transformation der (durch $p_\varrho x^\varrho = 0$ charakteri-

[1]) Zur Differentialgeometrie der Gruppe der Berührungstransformationen, I Doppelthomogene Behandlung von Berührungstransformationen, Proc. Royal Acad. Amsterdam.

sierten) Elemente zu ändern, ersetzen können durch eine Transformation, die ausser (1) und (2) auch für den allgemeinen Fall $p_\varrho x^\varrho \neq 0$ der Bedingung (3) und somit auch (4) genügt. Die so erhaltene Form nennen wir *eine Normalform* der doppelthomogenen Berührungstransformation. Wir bringen den Beweis in einer solchen Weise, dass sich dabei das Haupttheorem bezüglich der allgemeinsten Form einer endlichen doppelthomogenen Berührungstransformation mit ergibt.

2. *Die Normalform.*

Die allgemeinste Form einer homogenen Berührungstransformation in $\xi^1, \ldots, \xi^n, \eta_1, \ldots, \eta_n$ bekommt man nach LIE [1]) in folgender Weise. Man wähle irgendwelche Funktionen $\overset{1}{\Omega}, \ldots, \overset{q}{\Omega}$ der ξ^h und $\xi^{h'}$ (wo q irgend eine Zahl $\geqq 1$ und $\leqq n$ ist), die dermassen beschaffen sind, dass die $(n+q)$-reihige Determinante

$$\begin{vmatrix} \partial_i \overset{\alpha}{\Omega}, & 0 \\ \lambda \partial_i \partial_{i'} \overset{\alpha}{\Omega}, & \partial_{i'} \overset{\alpha}{\Omega} \\ \alpha & \end{vmatrix}; \alpha = 1, \ldots, q; \partial_i = \frac{\partial}{\partial \xi^i}, \partial_{i'} = \frac{\partial}{\partial \xi^{i'}}; \quad . \quad . \quad (5)$$

nicht vermöge $\overset{\alpha}{\Omega} = 0$ identisch in den $\underset{\alpha}{\lambda}$ verschwindet und eliminiere die $\underset{\alpha}{\lambda}$ aus den $2n+q$ Gleichungen

$$\overset{\alpha}{\Omega}(\xi^h, \xi^{h'}) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$a) \quad \eta_i = -\underset{\alpha}{\lambda} \partial \overset{\alpha}{\Omega}; \qquad b) \quad \eta_{i'} = +\underset{\alpha}{\lambda} \partial_{i'} \overset{\alpha}{\Omega}. \quad . \quad . \quad . \quad . \quad (7)$$

Die Determinantenbedingung verbürgt, dass sich die Gleichungen (6, 7) sowohl nach $\xi^{h'}, \eta_{i'}$ und $\underset{\alpha}{\lambda}$ als auch nach $\xi^h, \eta_i, \underset{\alpha}{\lambda}$ lösen lassen. Aus (6, 7*a*) ergeben sich nach Fortschaffung der $\underset{\alpha}{\lambda}$ die $\xi^{h'}$ als Funktionen der ξ^h und der η_i, homogen nullten Grades in η_i. Setzt man diese Werte in (7*a*) ein, so ergeben sich die $\underset{\alpha}{\lambda}$ als Funktionen der ξ^h und η_i, homogen ersten Grades in η_i. Substitution der $\xi^{h'}$ und der $\underset{\alpha}{\lambda}$ in (7*b*) ergibt schliesslich die $\eta_{i'}$ als Funktionen der ξ^h und η_i, homogen ersten Grades in η_i. Das selbe gilt bei Vertauschung von $\xi^{h'}, \eta_{i'}$ mit ξ^h, η_i (LIE, a.a.O., S. 152). Elimination der $\underset{\alpha}{\lambda}$ ergibt also ein System von $2n$ Gleichungen, dass sowohl nach $\xi^{h'}, \eta_{i'}$ als nach ξ^h, η_i auflösbar ist. Diese Gleichungen stellen eine Berührungstransformation dar, die einen Punkt allgemeiner Lage in eine $(n-q)$-dimensionale Mannigfaltigkeit überführt, und es gibt ausser den (6) keine weiteren Gleichungen zwischen $\xi^h, \xi^{h'}$ (LIE, a.a.O., S. 168). Der Rang der Matrix $\frac{\partial \xi^{h'}}{\partial \eta_i}$ ist also gleich $n-q$.

[1]) Theorie der Transformationsgruppen, II, 150.

Wir machen jetzt den Uebergang zu den homogenen Koordinaten $x^\varkappa, p_\lambda$; $\varkappa, \lambda, \mu = 0, 1, \ldots, n$, der Elemente $(p_\varrho x^\varrho = 0)$

$$\left.\begin{aligned} &x^0 : x^1 : \ldots : x^n = 1 : \xi^1 : \ldots : \xi^n \\ &p_0 : p_1 : \ldots : p_n = -(\xi^1 \eta_1 + \ldots + \xi^n \eta_n) : \eta_1 : \ldots : \eta_n \end{aligned}\right\} \quad . \quad . \quad (8)$$

wodurch (6) übergeht in

$$\overset{\mathfrak{a}}{\Phi}(x^\varkappa, x^{\varkappa'}) = \overset{\mathfrak{a}}{\Omega}\left(\frac{x^\alpha}{x^0}, \frac{x^{\alpha'}}{x^{0'}}\right) = 0 \; . \; . \; . \; . \; . \; . \quad (9)$$

wo die $\overset{\mathfrak{a}}{\Phi}$ homogen nullten Grades in $x^\varkappa$ und in $x^{\varkappa'}$ sind, und (7) in

$$\left.\begin{aligned} -\frac{p_\alpha}{p_0 x^0}(\xi^j \eta_j) &= -\underset{\mathfrak{a}}{\lambda}\partial_\alpha \overset{\mathfrak{a}}{\Phi}; & -\frac{p_{\alpha'}}{p_{0'} x^{0'}}(\xi^{j'} \eta_{j'}) &= +\underset{\mathfrak{a}}{\lambda}\partial_{\alpha'} \overset{\mathfrak{a}}{\Phi}; \\ -\frac{1}{x^0}(\xi^j \eta^j) &= -\underset{\mathfrak{a}}{\lambda}\partial_0 \overset{\mathfrak{a}}{\Phi}; & -\frac{1}{x^{0'}}(\xi^{j'} \eta_{j'}) &= +\underset{\mathfrak{a}}{\lambda}\partial_{0'} \overset{\mathfrak{a}}{\Phi}; \end{aligned}\right\} \quad \left\{\begin{aligned} &\alpha, \beta, \gamma = 1, \ldots, n; \\ &h, i, j = 1, \ldots, n; \\ &\partial_\lambda = \frac{\partial}{\partial x^\lambda}; \partial_{\lambda'} = \frac{\partial}{\partial x^{\lambda'}} \end{aligned}\right\} . \quad (10)$$

oder

$$p_\lambda : : -\underset{\mathfrak{a}}{\lambda}\partial_\lambda \overset{\mathfrak{a}}{\Phi}; \; p_{\lambda'} : : +\underset{\mathfrak{a}}{\lambda}\partial_{\lambda'} \overset{\mathfrak{a}}{\Phi} \; . \; . \; . \; . \; . \; . \quad (11)$$

aus welchen Proportionalitäten sich umgekehrt die Gleichungen (7) ableiten lassen. Die $\underset{\mathfrak{a}}{\lambda}$ lassen sich aus (6, 7) als Funktionen der ξ^h und η_i, homogen ersten Grades in η_i bestimmen. Da aber die Gleichung (8) nicht gestattet die η_i in die p_λ auszudrücken, sondern nur die Verhältnisse der η_i in die Verhältnisse der p_λ, lassen sich aus (9, 11) nur die Verhältnisse der $\underset{\mathfrak{a}}{\lambda}$ und zwar als homogene Funktionen nullten Grades in $x^\varkappa$ und in p_λ berechnen. Ausserdem lassen sich aus (6, 7) $\xi^{h'}$ und $\eta_{i'}$ als Funktionen von ξ^h und η_i homogen nullten bzw. ersten Grades in η_i berechnen. Aus (9, 11) folgen also die $\frac{x^{\varkappa'}}{x^{0'}}$ und die $-\frac{\eta_{i'}}{\xi^{j'} \eta_{j'}}$ oder, was dasselbe ist, die $\frac{p_{\lambda'}}{p_{0'}}$, als Funktionen der $\frac{x^\varkappa}{x^0}$ und der $\frac{p_\lambda}{p_0}$. Ebenso lassen sich die $\frac{x^\varkappa}{x^0}$ und die $\frac{p_\lambda}{p_0}$ als Funktionen der $\frac{x^{\varkappa'}}{x^{0'}}$ und $\frac{p_{\lambda'}}{p_{0'}}$ berechnen. Alle Gleichungen zusammenfassend bekommen wir also

$$\overset{\mathfrak{a}}{\Phi}(x^\varkappa, x^{\varkappa'}) = 0 \quad (\mathfrak{a} = 1, \ldots, q) \; . \; . \; . \; . \; . \; . \quad (12)$$

$$a) \; p_\lambda = -\underset{1}{\lambda}\partial_\lambda \frac{\overset{\lambda}{\underset{\mathfrak{a}}{}}}{\underset{1}{\lambda}} \overset{\mathfrak{a}}{\Phi}; \quad b) \; p_{\lambda'} = +\underset{1}{\lambda}\partial_{\lambda'} \frac{\overset{\lambda}{\underset{\mathfrak{a}}{}}}{\underset{1}{\lambda}} \overset{\mathfrak{a}}{\Phi} \; . \; . \; . \quad (13)$$

wo $\underset{1}{\lambda}$ jetzt die Rolle eines unbestimmten Proportionalitätsfaktor spielt, und

$$a) \; x^{\varkappa'} = \alpha \varphi^{\varkappa'}(x^\varkappa, p_\lambda); \quad b) \; p_{\lambda'} = \beta \psi_{\lambda'}(x^\varkappa, p_\lambda); \; . \; . \; . \quad (14)$$

$$a) \; x^\varkappa = \gamma \varphi^\varkappa(x^{\varkappa'}, p_{\lambda'}); \quad b) \; p_\lambda = \varepsilon \psi_\lambda(x^{\varkappa'}, p_{\lambda'}). \; . \; . \; . \quad (15)$$

Nach Elimination der Verhältnisse der λ ist $\frac{1}{\lambda}\overset{\alpha}{\lambda}\overset{\alpha}{\Phi}$ eine bekannte Funktion.

Die $q^{\varkappa'}$ und $\psi_{\lambda'}$ lassen sich homogen nullten Grades in $x^{\varkappa}$ und in p_λ fest wählen und die $\varphi^{\varkappa}$ und ψ_λ ebenso als Funktionen nullten Grades in $x^{\varkappa'}$ und $p_{\lambda'}$. Die Funktionen $\varphi^{\varkappa'}, \psi_{\lambda'}, \varphi^{\varkappa}, \psi_\lambda$ sind jetzt bekannt, nur die Koeffizienten $\alpha, \beta, \gamma, \varepsilon$ und $\overset{\lambda}{1}$ sind noch unbestimmt. Sind a, b bzw. c, d die Grade von α bzw. β in $x^{\varkappa}$ und p_λ und a', b' bzw. c', d' die Grade von γ bzw. ε in $x^{\varkappa'}$ und $p_{\lambda'}$ so folgt bei Substitution von (14) in (15)

$$a'e = d, \quad b'e = -b, \quad c'e = -c, \quad d'e = a; \ (e = ad - bc) \ . \quad (16)$$

und daraus folgt, das γ und ε durch die Wahl von α und β festgelegt sind, vorausgesetzt dass $ad - bc \neq 0$ ist. Ausserdem ist β durch α bestimmt infolge der Forderung

$$p_{\varrho'}\, dx^{\varrho'} = p_\varrho\, dx^{\varrho} \text{ für } p_\varrho\, x^{\varrho} = 0 \ . \ . \ . \ . \ . \ . \quad (17)$$

Setzt man (14*b*) und (14*a*) links bzw. rechts in (13*b*) ein, so lässt sich $\overset{\lambda}{1}$ aus dieser Gleichung als homogene Funktion von $x^{\varkappa}$ und p_λ von den Graden $a + c, b + d$ berechnen. Die Wahl von α legt also *alle* Koeffizienten fest. Wir wollen diese Wahl so treffen dass $a = 1$, $b = 0$ wird und demzufolge $c = 0$, $d = 1$, $a' = 1$, $b' = 0$, $c' = 0$, $d' = 1$. Dazu brauchen wir nur für α eine beliebige homogene Funktion von $x^{\varkappa}$ und p_λ von den Graden $+1, 0$ zu wählen. $\overset{\lambda}{1}$ bekommt dann die Grade $+1, +1$ in $x^{\varkappa}$ und p_λ und dieselben Grade beim Ausschreiben in $x^{\varkappa'}$ und $p_{\lambda'}$.

Setzen wir jetzt (13*a*) rechts in (14*a*) ein, so ergibt sich

$$\left.\begin{aligned} x^{\varkappa'} = \alpha\,(x^{\varkappa}, -\partial_\lambda \overset{\alpha}{\lambda}\overset{\alpha}{\Phi}) \,.\, \varphi^{\varkappa'}(x^{\varkappa}, -\partial_\lambda \overset{\alpha}{\lambda}\overset{\alpha}{\Phi}) = \\ = \alpha\,(x^{\varkappa}, -\overset{\alpha}{\lambda}\partial_\lambda \overset{\alpha}{\Phi}) \,.\, \varphi^{\varkappa'}(x^{\varkappa}, -\overset{\alpha}{\lambda}\partial_\lambda \overset{\alpha}{\Phi}) \end{aligned}\right\} \ . \ . \ . \ . \quad (18)$$

und dies ein System von $n+1$ Gleichungen in $x^{\varkappa}$ und $x^{\varkappa'}$, das q Parameter $\overset{\alpha}{\lambda}\,(\alpha = 1, \ldots, q)$ enthält und zwar homogen nullten Grades. Aus $q-1$ von diesen Gleichungen lassen sich die Verhältnisse dieser Parameter als Funktionen der $x^{\varkappa}$ und $x^{\varkappa'}$ bestimmen. Setzt man diese Werte in die übrigen $n-q+2$ Gleichungen ein, so erfolgt aus dem Umstande, dass die $\overset{\alpha}{\lambda}$ homogen nullten Grades vorkommen, dass die rechten Seiten homogen von den Graden $+1$, 0 in $x^{\varkappa}$ und $x^{\varkappa'}$ werden und sich also $n-q+2$ Gleichungen von der Form

$$\overset{\alpha}{X}(x^{\varkappa}, x^{\varkappa'}) = 1 \qquad (\alpha = q-1, \ldots n) \ . \ . \ . \ . \ , \quad (19)$$

ergeben, deren linke Seiten von den Graden $+1, -1$ in $x^{\varkappa}, x^{\varkappa'}$ sind. Da der Quotient zweier X eine homogene Funktion von den Graden 0,0 in $x^{\varkappa}$ und $x^{\varkappa'}$ darstellt, und es nur q homogene Gleichungen nullten

Grades in $x^{\varkappa}$ und $x^{\varkappa'}$ geben kann, nämlich (12), lassen sich sicher $n-q+1$ von den Gleichungen (19) aus der $(n-q+2)$-ten und (12) ableiten. Diese $(n-q+2)$-te Gleichung ist aber sicher von (12) unabhängig, da sie von den Graden $+1, -1$ in $x^{\varkappa}, x^{\varkappa'}$ ist. Diese Gleichung schreiben wir

$$X(x^{\varkappa}, x^{\varkappa'}) = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Die q homogenen Gleichungen (12) ordnen jedem Punkt allgemeiner Lage in der H_n eine $(n-q)$-dimensionale Mannigfaltigkeit zu. Die Gleichung (20) ändert daran nichts, sie legt nur den Faktor in den $x^{\varkappa'}$ fest. Für die geometrische Transformation der Elemente hat also (20) keine Bedeutung, was auch eigentlich selbstverständlich ist, da sie erst entstanden ist nach Festlegung der Wahl von α, die ja ebenfalls für die geometrische Transformation der Elemente unwesentlich ist. Der Rang der Matrix von $\dfrac{\partial x^{\varkappa'}}{\partial p_\lambda}$ wird $n-q$, also gleich dem Range der Matrix von $\dfrac{\partial \xi^{h'}}{\partial \eta_i}$.

Die Gleichung (20) ermöglicht uns nun unsere Aufgabe zu erfüllen und die Berührungstransformation (14, 15) durch eine andere zu ersetzen, die in bezug auf Elemente genau so wirkt wie (14, 15) aber den Gleichungen (1), (2) und (3) auch für $p_\varrho x^\varrho \neq 0$ genügt. Führen wir nämlich statt der Gleichungen (13) die Gleichungen

$$p_\lambda = -\underset{\alpha}{\lambda}\,\partial_\lambda \overset{\alpha}{\Phi} + p_{\varrho'} x^{\varrho'}\,\partial_\lambda X\,; \quad p_{\lambda'} = +\underset{\alpha}{\lambda}\,\partial_{\lambda'} \overset{\alpha}{\Phi} - p_\varrho x^\varrho\,\partial_{\lambda'} X \quad . \quad (21)$$

ein, die für Elemente mit (13) identisch werden, so ist erstens

$$\left.\begin{aligned} x^{\varrho'} p_{\varrho'} &= 0 + p_\varrho x^\varrho X = p_\varrho x^\varrho \\ x^\varrho p_\varrho &= 0 + p_{\varrho'} x^{\varrho'} X = p_{\varrho'} x^{\varrho'} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

zweitens, mit Berücksichtigung von (22)

$$-p_\varrho\,dx^\varrho + p_{\varrho'}\,dx^{\varrho'} = -p_\varrho x^\varrho\,dX = 0, \quad . \quad . \quad . \quad . \quad (23)$$

und zwar auch für $p_\varrho x^\varrho \neq 0$ und aus (22) und (23) folgt, ebenfalls für alle Fälle,

$$x^{\varrho'}\,dp_{\varrho'} = x^\varrho\,dp_\varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Wir nennen (21) *eine Normalform* der doppelthomogenen Berührungstransformation. Da die Wahl von α beliebig ist, ist die Normalform nicht eindeutig bestimmt. Da die Form von X von der Wahl von α abhängt, kann man auch umgekehrt anfangen und X als Funktion von $x^{\varkappa}$ und $x^{\varkappa'}$ der Grade $+1, -1$ beliebig wählen.

3. *Das Haupttheorem.*
Setzen wir

$$\left.\begin{aligned} X = \overset{0}{X};\ X(\overset{a}{\Phi}+1) &= \overset{a}{X} \\ \underset{a}{\lambda} = X\,\underset{a}{\mu};\ p_\varrho\, x^\varrho + \underset{a}{\mu}\,\frac{\overset{a}{X}}{\overset{a}{X}} &= -\underset{0}{\mu} \end{aligned}\right\} \quad \ldots\ldots \quad (25)$$

so werden die $\overset{p}{X}.\ (p = 0, 1, \ldots, q)$ homogen von den Graden $+1, -1$ in $x^\varkappa, x^{\varkappa'}$ und die Gleichungen (12), (20) und (21) lassen sich schreiben

$$\overset{p}{X}(x^\varkappa, x^{\varkappa'}) = 1; \quad (p = 0, 1, \ldots, q) \quad \ldots\ldots \quad (26)$$

$$p_\lambda = -\underset{p}{\mu}\,\partial_\lambda \overset{p}{X}; \quad p_{\lambda'} = +\underset{p}{\mu}\,\partial_{\lambda'} \overset{p}{X}. \quad \ldots\ldots \quad (27)$$

Die Berührungstransformation wird erhalten durch Elimination der $\underset{p}{\mu}$ und Lösung von (26), (27) nach $x^{\varkappa'}, p_{\lambda'}$ sowie nach $x^\varkappa, p_\lambda$. Es fragt sich nun ob man umgekehrt aus $q+1$ beliebigen homogenen Funktionen der Grade $+1, -1$ in $x^\varkappa, x^{\varkappa'}$ in dieser Weise stets eine doppelthomogene Berührungstransformation mit den Graden $+1,0;\ 0, +1$ bekommt. Erstens müssen sich die Gleichungen natürlich nach $x^{\varkappa'}, p_{\lambda'}, \underset{p}{\mu}$ und ebenfalls nach $x^\varkappa, p_\lambda, \underset{p}{\mu}$ lösen lassen, d.h. die Determinante

$$\begin{vmatrix} \partial_\lambda \overset{p}{X}, & 0 \\ \underset{p}{\mu}\,\partial_{\lambda'}\partial_\lambda \overset{p}{X}, & \partial_{\lambda'} \overset{p}{X} \end{vmatrix} \quad \ldots\ldots\ldots \quad (28)$$

darf nicht infolge (26) identisch in $\underset{p}{\mu}$ verschwinden. Ist diese Forderung erfüllt, so ergibt sich nach LIE jedenfalls eine homogene Berührungstransformation und die Grade von $x^{\varkappa'}$ und $p_{\lambda'}$ in p_λ werden 0 bzw. $+1$. Da wir von homogenen Funktionen in $x^\varkappa, x^{\varkappa'}$ ausgingen ist die Transformation auch doppelthomogen und es muss also nur noch bewiesen werden, dass die Grade von $x^{\varkappa'}$ und $p_{\lambda'}$ in $x^\varkappa$ bzw. $+1$ und 0 werden. Sind die durch Lösung nach $x^{\varkappa'}, p_{\lambda'}$ erhaltenen Gleichungen und ihre Umkehrungen

$$a)\ x^{\varkappa'} = \varphi^{\varkappa'}(x^\varkappa, p_\lambda); \qquad b)\ p_{\lambda'} = \psi_{\lambda'}(x^\varkappa, p_\lambda); \quad \ldots \quad (29)$$

$$a)\ x^\varkappa = \varphi^\varkappa(x^{\varkappa'}, p_{\lambda'}); \qquad b)\ p_\lambda = \psi_\lambda(x^{\varkappa'}, p_{\lambda'}); \quad \ldots \quad (30)$$

so folgt aus dem Umstande, dass man die linke Seite der Gleichungen (26) auch homogen von den Graden $-1, +1$ in $x^\varkappa, x^{\varkappa'}$ schreiben kann, dass die Grade von (29) und (30) gleich sein müssen also (vergl. S. 239)

$$a = a',\ b = b' = 0,\ c = c',\ d = d' = 1 \quad \ldots\ldots \quad (31)$$

Aus (16) folgt dann entweder

$$a = a' = +1,\ c = c' = 0 \quad \ldots\ldots\ldots \quad (32)$$

oder

$$a = a' = -1,\ c = c' = \text{frei wählbar} \quad \ldots\ldots \quad (33)$$

Nehmen wir nun an es sei $a = -1$ so wäre

$$\frac{x^{\varkappa'}}{x^{0'}}\, x^0\, x^{0'} = \varphi^{\varkappa'}\left(\frac{x^\varkappa}{x^0}, p_\lambda\right) \quad \ldots\ldots\ldots \quad (34)$$

und die Elimination der p_λ könnte also nur Gleichungen ergeben, die $\frac{x^{\varkappa'}}{x^{0'}}$, $\frac{x^\varkappa}{x^0}$ und $x^0\, x^{0'}$ enthielten, also Gleichungen von der Form

$$\frac{1}{x^0\, x^{0'}} F\left(\frac{x^{\varkappa'}}{x^{0'}}, \frac{x^\varkappa}{x^0}\right) = 1 \quad \ldots\ldots\ldots \quad (35)$$

Das System dieser Gleichungen müsste mit (26) gleichwertig sein. Nun sind aber jene Gleichungen homogen nullten Grades in den $2n+2$ Variablen $x^\varkappa, x^{\varkappa'}$ und folglich kann ein System von Gleichungen der Form (35) niemals mit (26) gleichwertig sein. Es bleiben also nur die Werte (32).

Damit haben wir folgenden Satz bewiesen:

Hauptsatz.

Die allgemeinste doppelthomogene Berührungstransformation von $x^\varkappa, p_\lambda$ in $x^{\varkappa'}, p_{\lambda'}$ von den Graden 1,0 bzw. 0,1 in $x^\varkappa$ und p_λ in der Normalform wird erhalten, indem man ausgeht von $q+1$ $(1 \leqq q \leqq n)$ Gleichungen von der Form (26), *wo die* $\overset{\mathfrak{p}}{X}$ *homogene Funktionen von $x^\varkappa, x^{\varkappa'}$ von den Graden $+1, -1$ sind, so gewählt, dass die Determinante* (28) *infolge* (26) *nicht identisch in den* $\overset{\mathfrak{p}}{\mu}$ *verschwindet und sodann die* $\overset{\mathfrak{p}}{\mu}$ *aus den Gleichungen* (26) *und* (27) *eliminiert und diese Gleichungen nach $x^{\varkappa'}, p_{\lambda'}$ bzw. $x^\varkappa, p_\lambda$ auflöst.*

Da vollkommener Dualismus besteht zwischen den $x^\varkappa$ und den p_λ, kann man bei der Formulierung des Hauptsatzes $x^\varkappa$ und p_λ vertauschen. Man kann also ebensogut mit Funktionen von $p_\lambda, p_{\lambda'}$ von den Graden $+1, -1$ anfangen.

4. *Beispiel.*

Der Weg um von einer homogenen Berührungstransformation zu einer der zugehörigen doppelthomogenen zu gelangen ist recht einfach. Man schreibt zunächst die Funktionen $\overset{\mathfrak{a}}{\Phi}$ in $x^\varkappa$ und $x^{\varkappa'}$, wählt eine beliebige Funktion X von den Graden $+1, -1$ in $x^\varkappa$ und $x^{\varkappa'}$ und bildet dann die $\overset{\mathfrak{p}}{X}$.

Als Beispiel behandeln wir die Transformation

$$\left.\begin{aligned} &\xi^{1'} = \xi^1 - \xi^a\,\zeta_a; \quad \xi^{2'} = \zeta_2; \quad \xi^{3'} = \zeta_3; \\ &\zeta_{2'} = -\xi^2; \quad \zeta_{3'} = -\xi^3 \end{aligned}\right\} \quad (a = 2, 3) \ldots \quad (36)$$

Uebergang zu ξ^h, η_i ergibt die Transformation

$$\left.\begin{aligned} &\xi^{a'} = -\frac{\eta_a}{\eta_1}; \quad \eta_{a'} = \xi^a\,\eta_1; \\ &\xi^{1'} = \frac{\xi^j\,\eta_j}{\eta_1}; \quad \eta_{1'} = \eta_1; \end{aligned}\right\} \quad (h, i, j = 1, 2, 3) \ldots \quad (37)$$

die durch die Forderung $\eta_{j'}\,d\xi^{j'} = \eta_j\,d\xi^j$ eindeutig festgelegt ist. Es gibt nur eine Funktion Ω, nämlich

$$\Omega \equiv \xi^{1'} - \xi^1 + \xi^2\,\xi^{2'} + \xi^3\,\xi^{3'} = 0 \ldots \quad (38)$$

die beim Uebergang zu $x^\varkappa, p_\lambda$ übergeht in

$$\Phi \equiv \frac{x^{1'}}{x^{0'}} - \frac{x^1}{x^0} + \frac{x^2\,x^{2'}}{x^0\,x^{0'}} + \frac{x^3\,x^{3'}}{x^0\,x^{0'}} = 0 \ldots \quad (39)$$

Wir bekommen also die Gleichungen

$$\left.\begin{aligned} &p_0 = -\lambda\frac{x^{1'}}{x^0\,x^{0'}} + \lambda\frac{\Phi}{x^0} = -\lambda\frac{x^{1'}}{x^0\,x^{0'}}; \quad p_{0'} = -\lambda\frac{x^1}{x^0\,x^{0'}} + \lambda\frac{\Phi}{x^{0'}} = -\lambda\frac{x^1}{x^0\,x^{0'}}; \\ &p_1 = \lambda\frac{1}{x^0}; \quad p_{1'} = \lambda\frac{1}{x^{0'}}; \\ &p_2 = -\lambda\frac{x^{2'}}{x^0\,x^{0'}}; \quad p_{2'} = \lambda\frac{x^2}{x^0\,x^{0'}}; \\ &p_3 = -\lambda\frac{x^{3'}}{x^0\,x^{0'}}; \quad p_{3'} = \lambda\frac{x^3}{x^0\,x^{0'}}; \end{aligned}\right\} \quad \begin{matrix} a) \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} b) \\ \\ \\ \\ \\ \end{matrix} \quad . \quad (40)$$

(wobei in der ersten Zeile von der Gleichung $\Phi = 0$ Gebrauch gemacht ist) und aus diesen Gleichungen ergibt sich

$$\left.\begin{aligned} &x^{0'} = \alpha; \quad p_{0'} = -\beta\frac{x^1}{x^0}; \quad x^0 = \gamma; \quad p_0 = -\delta\frac{x^{1'}}{x^{0'}}; \\ &x^{1'} = -\alpha\frac{p_0}{p_1}; \quad p_{1'} = \beta; \quad x^1 = -\gamma\frac{p_{0'}}{p_{1'}}; \quad p_1 = \delta; \\ &x^{2'} = -\alpha\frac{p_2}{p_1}; \quad p_{2'} = \beta\frac{x^2}{x^0}; \quad x^2 = \gamma\frac{p_{2'}}{p_{1'}}; \quad p_2 = -\delta\frac{x^{2'}}{x^{0'}}; \\ &x^{3'} = -\alpha\frac{p_3}{p_1}; \quad p_{3'} = \beta\frac{x^3}{x^0}; \quad x^3 = \gamma\frac{p_{3'}}{p_{1'}}; \quad p_3 = -\delta\frac{x^{3'}}{x^{0'}}. \end{aligned}\right\} \quad \begin{matrix} a) \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} b) \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} c) \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} d) \\ \\ \\ \\ \\ \end{matrix} \quad . \quad (41)$$

γ und δ lassen sich als Funktionen von $x^{\varkappa'}, p_{\lambda'}$ bestimmen sobald α und

β als Funktionen von $x^\varkappa$ und p_λ gegeben sind, vorausgesetzt, das $ad - bc \neq 0$ ist (vgl. S. 239). Wir bestimmen β aus α, indem wir fordern

$$p_{\varrho'}\, dx^{\varrho'} = p_\varrho\, dx^\varrho = -\, x^\varrho\, dp_\varrho \qquad (\varrho = 0, 1, 2, 3) \quad . \quad . \quad . \quad (42)$$

oder (unter Berücksichtigung von $p_\varrho\, x^\varrho = 0$):

$$\left.\begin{aligned} \beta\, d\alpha \left(-\frac{x^1}{x^0} - \frac{p_0}{p_1} - \frac{p_2 x^2}{p_1 x^0} - \frac{p_3 x^3}{p_1 x^0} \right) + \beta\alpha \left(-\frac{1}{p_1}\, dp_0 + \frac{p_0}{(p_1)^2} \right) dp_1 \\ - \frac{x^2}{p_1 x^0}\, dp_2 + \frac{p_2 x^2}{(p_1)^2 x^0}\, dp_1 - \frac{x^3}{p_1 x^0}\, dp_3 + \frac{p_3 x^3}{(p_1)^2 x^0}\, dp_1 = \\ = -\frac{\beta\alpha}{p_1 x^0}\, x^\varrho\, dp_\varrho = -\, x^\varrho\, dp_\varrho \end{aligned}\right\} \quad . \quad (43)$$

woraus folgt

$$\alpha\beta = +\, p_1 x^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Ebenso findet man

$$\gamma\delta = +\, p_{1'} x^{0'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

und durch Substitution von (41, *a*, *b*) in (40*b*)

$$\lambda = \alpha\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

und ebenso durch Substitution von (41, *c*, *d*) in (40*a*)

$$\lambda = \gamma\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Wählen wir jetzt für α irgend eine Funktion von $x^\varkappa$ und p_λ von den Graden 1,0 z.B. $\alpha = x^0$ so folgt

$$\alpha = x^0,\ \beta = p_1,\ \gamma = x^{0'},\ \delta = p_1;\ \lambda = p_1 x^0 = p_{1'} x^{0'} \quad . \quad . \quad (48)$$

und

$$\left.\begin{array}{llll} x^{0'} = x^0\ ; & p_{0'} = -\frac{p_1 x^1}{x^0}; & x_0 = x^{0'}\ ; & p_0 = -\frac{p_{1'} x^{1'}}{x^{0'}} \\ x^{1'} = -\frac{p_0 x^0}{p_1}; & p_{1'} = p_1\ ; & x^1 = -\frac{p_{0'} x^{0'}}{p_{1'}}; & p_1 = p_{1'} \\ x^{2'} = -\frac{p_2 x^0}{p_1}; & p_{2'} = \frac{p_1 x^2}{x^0}; & x^2 = \frac{p_{2'} x^{0'}}{p_{1'}}; & p_2 = -\frac{p_{1'} x^{2'}}{x^{0'}} \\ x^{3'} = -\frac{p_3 x^0}{p_1}; & p_{3'} = \frac{p_1 x^3}{x^0}; & x^3 = \frac{p_{3'} x^{0'}}{p_{1'}}; & p_3 = -\frac{p_{1'} x^{3'}}{x^{0'}} \end{array}\right\} \quad (49)$$

a) b) c) d)

Die Gleichung (20) ist hier

$$\frac{x^0}{x^{0'}} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

sodass wir zur verallgemeinerten Transformation

$$\left.\begin{array}{llll} p_0 = -\lambda \dfrac{x^{1'}}{x_0\, x^{0'}} + p_{\varrho'}\, x^{\varrho'} \dfrac{1}{x^{0'}}; & p_{0'} = -\lambda \dfrac{x^1}{x^0\, x^{0'}} + p_\varrho\, x^\varrho \dfrac{1}{x^{0'}}; & & \\ p_1 = \lambda \dfrac{1}{x^0}; & p_{1'} = \lambda \dfrac{1}{x^{0'}}; & & \\ p_2 = -\lambda \dfrac{x^{2'}}{x^0\, x^{0'}}; & p_{2'} = \lambda \dfrac{x^2}{x^0\, x^{0'}}; & & \\ p_3 = -\lambda \dfrac{x^{3'}}{x^0\, x^{0'}}; & p_{3'} = \lambda \dfrac{x^3}{x^0\, x^{0'}}; & & \end{array}\right\} \quad . \quad . \quad . \quad (51)$$

gelangen. Wegen $\lambda = p_1\, x^0$ ergibt sich

$$\left.\begin{array}{llll} x^{0'} = x^0; & p_{0'} = p_0 + \dfrac{p_2 x^2 + p_3 x^3}{x^0}; & x^0 = x^{0'}; & p_0 = p_{0'} + \dfrac{p_{2'} x^{2'} + p_{3'} x^{3'}}{x^{0'}}; \\ x^{1'} = x^1 + \dfrac{p_2 x^2 + p_3 x^3}{p_1}; & p_{1'} = p_1; & x^1 = x^{1'} + \dfrac{p_{2'} x^{2'} + p_{3'} x^{3'}}{p_{1'}}; & p_1 = p_{1'}; \\ x^{2'} = -\dfrac{p_2\, x_0}{p_1}; & p_{2'} = \dfrac{p_1\, x^2}{x^0}; & x^2 = \dfrac{p_{2'} x^{0'}}{p_{1'}}; & p_2 = -\dfrac{p_{1'} x^{2'}}{x^{0'}}; \\ x^{3'} = -\dfrac{p_3\, x^2}{p_1}; & p_{3'} = \dfrac{p_1\, x^3}{x^0}; & x^3 = \dfrac{p_{3'} x^{0'}}{p_{1'}}; & p_3 = -\dfrac{p_{1'} x^{3'}}{x^{0'}}; \end{array}\right\} \quad (52)$$

und für diese Transformation, die auf Elemente ($p_\varrho\, x^\varrho = 0$) angewandt mit (49) identisch wird, gelten nun tatsächlich die Gleichungen (2), (3) (4) auch für $p_\varrho\, x^\varrho \neq 0$. Man erhält die also gefundene Normalform auch, wenn man die Gleichungen

$$\left.\begin{array}{l} \overset{0}{X} \equiv \dfrac{x^0}{x^{0'}} = 1; \quad \overset{1}{X} \equiv \dfrac{1}{(x^{0'})^2}(x^0 x^{1'} - x^1 x^{0'} + x^2 x^{2'} + x^3 x^{3'} + x^0 x^{0'}) = 1, \\ \\ p_0 = -\underset{0}{\mu} \dfrac{1}{x^{0'}} - \underset{1}{\mu} \dfrac{x^{0'} + x^{1'}}{(x^{0'})^2}; \quad p_{0'} = -\dfrac{\underset{0}{\mu}}{x^{0'}} - \underset{1}{\mu} \dfrac{x^0 + x^1}{(x^{0'})^2}; \\ p_1 = -\underset{1}{\mu} \dfrac{1}{x^{0'}}; \quad p_{1'} = \underset{1}{\mu} \dfrac{1}{x^{0'}}; \\ p_2 = -\underset{1}{\mu} \dfrac{x^{2'}}{(x^{0'})^2}; \quad p_{2'} = \underset{1}{\mu} \dfrac{x^2}{(x^{0'})^2}; \\ p_3 = -\underset{1}{\mu} \dfrac{x^{3'}}{(x^{0'})^2}; \quad p_{3'} = \underset{1}{\mu} \dfrac{x^3}{(x^{0'})^2}; \end{array}\right\} \quad (53)$$

nach Elimination von $\underset{0}{\mu}$ und $\underset{1}{\mu}$ nach $x^{\varkappa'}, p_{\lambda'}$ und nach $x^\varkappa, p_\lambda$ löst.

Chemistry. — *Investigations on the Complex Salts of the Racemic and Optically active Cyclohexanediamines with trivalent Cobaltum and Rhodium.* **III.** *Tri-Cyclohexanediamine Salts of trivalent Cobaltum.* By F. M. JAEGER and L. BIJKERK.

(Communicated at the meeting of February 27, 1937).

§ 1. The racemic *cyclohexanediamine* as well as its optically active components [1]) can be used in the preparation of the *cobaltic* salts; the corresponding products will be indicated in this paper as (*r-Chxn*)-, (*d-Chxn*)- or (*l-Chxn*) salts respectively. The preparation of the *tri-cyclohexanediamine* salts of this series always has to occur via the corresponding *praseo-* (or *violeo*)-salts of the type: $\left\{ Co \begin{matrix} (Chxn)_2 \\ Cl_2 \end{matrix} \right\} Cl$. The preparation of the latter is the same, whether one starts from the racemic or from the optically active bases. 30 Grammes of hydrated *cobaltous chloride* : $CoCl_2 + 6H_2O$ are dissolved in 110 cm³ water and the solution cooled to 15° C. It then is brought into a big ERLENMEYER-flask of 3 liters volume and mixed with 27,6 grammes of *cyclohexanediamine*: a pink precipitate is formed which in contact with the air rapidly assumes a dark brown colour. Under continuous shaking of the liquid now 240 cm³ of a 10 % solution of hydrogen peroxide are very slowly added from a dropping funnel; the temperature of the mixture gradually rises to about 40° C., while the colour of the liquid turns into a dark brown and a rather voluminous froth is continuously formed, filling the whole space of the vessel. After all hydrogen peroxide has been added and the original precipitate has completely vanished, a reddish-brown, clear solution remains, which is left standing for some hours and then is heated on the waterbath for the purpose of completing the reaction and destroying the peroxide still present. Sometimes a small quantity of a pale pink precipitate is formed thereby, which, however, disappears on addition of 450 cm³ of strong (1,19) hydrochloric acid. The acid solution now is evaporated to dryness on the water-bath, the dark green residue thus obtained repeatedly treated with absolute alcohol, and the alcoholic solutions each time completely evaporated. The final residue then is dried in a vacuum-exsiccator over *CaO* during several days, until all traces of hydrochloric acid still present are removed as completely as possible. The viscous, dark green mass then is repeatedly extracted by means of boiling absolute alcohol, the bluish-green extract filtered and evaporated, till a syrupy green mass is obtained, which is dried in vacuo over *CaO*. The *praseo*-salt (97 % of the theoretical yield) thus obtained is a dark green, *very hygroscopic* mass, which cannot be obtained in an absolutely pure state, nor in a well crystallized form.

[1]) F. M. JAEGER and L. BIJKERK, these Proceed., **40**, 12 (1937).

During the oxidation, moreover, about 5—6 % of a dark brown, peculiarly smelling organic substance is generated, which also dissolves in the alcohol used. A black residue, obtained on filtering off the alcoholic extracts, is repeatedly washed with absolute alcohol and then dissolved in an excess of boiling water; it chiefly consists of the corresponding *tri-cyclohexane-diamine* salt simultaneously formed, which, after filtering and evaporating, is obtained from its aqueous solution and can finally be recrystallized from boiling water. In this way 31 grammes of the *praseo*-compound and 3 grammes of the *tri-cyclohexanediamine* salt were isolated. The green *praseo*-salt dissolves in water to a reddish solution, most probably because of its being immediately transformed into the *diaquo*-salt.

§ 2. The corresponding *tri-cyclohexanediamine-cobaltic chloride* can be obtained from the green mass by boiling its solution in water during three hours with the calculated quantity of the base at a reflux-cooler provided with a tube filled with sodium- and calcium hydroxides. As the salt formed is only sparely soluble, a sufficient quantity of water must be added, so as to prevent too much bumping of the boiling liquid.

The warm salt-solution then is filtered off from a little of a black residue, evaporated on the water-bath, and the *chloride* obtained recrystallized from boiling water. The salt crystallizes in beautiful, fine needles of the composition:

$$\{Co(r\text{-}Chxn)_3\}Cl_3 + 1H_2O.$$

Analysis: 20,2 % *Cl*; 15,91 % *N*; 3,37 % H_2O; calculated: 20,27 % *Cl*; 15,99 % *N*; 3,42 % H_2O.

This *racemic compound*: $r\text{-}\{Co(Chxn)_3\}Cl_3 + 1H_2O$ crystallizes from a hot aqueous solution, on cooling, in long, yellow- or orange-red, lustrous, but very brittle thin needles, which usually only show an incomplete number of terminal faces. They are *ditetragonal-bipyramidal*; this was, moreover, corroborated by a LAUE-diagram on {001}. The axial ratio is: $a : c = 1 : 0{,}7212$. Some crystals were measured by means of the theodolite-goniometer (by Mr. TER BERG), the others by the aid of the usual one-circle-goniometer.

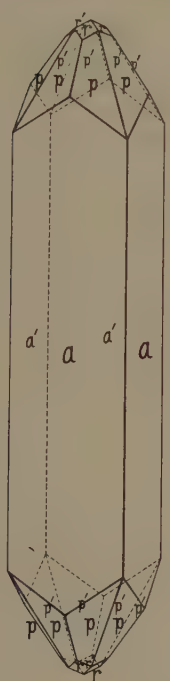


Fig. 1. *Crystalform of racemic* $\{Co(Chxn)_3\}Cl_3 + 1H_2O$

Forms observed: $a = \{100\}$, well developed and lustrous; $r = \{101\}$, small, but yielding good reflections; $p = \{211\}$, well developed, although mostly present with only part of its faces; $s = \{443\}$, small, giving good reflections; $t = \{337\}$, very narrow, but well measurable. The habitus is long-prismatic parallel to {100}. (Fig. 1).

Angular Values:	*Observed:*	*Calculated:*
$a:r = (100):(101) =$	*54° 12′	—
$r:r = (101):(011) =$	48 34	48° 52′
$a:p = (100):(211) =$	40 24	40 31
$a:p = (010):(211) =$	67 28	67 39
$c:p = (001):(211) =$	57 32	58 12
$p:p = (211):(121) =$	30 48	31 11
$s:t = (443):(337) =$	29 35	30 3
$s:c = (443):(001) =$	—	53 40
$t:t = (337):(\bar{3}\bar{3}7) =$	47 38	47 14
$s:a = (443):(010) =$	55 20	55 16½
$c:r = (001):(101) =$	35 48	35 48

A distinct cleavability could not be observed.

§ 3. The corresponding *bromide:* $\{Co(r\text{-}Chxn)_3\}Br_3 + 1H_2O$ *(with* 2,69 % H_2O; calculated: 2,73 %) is even less soluble than the chloride. Thusfar it could not yet be obtained in measurable crystals.

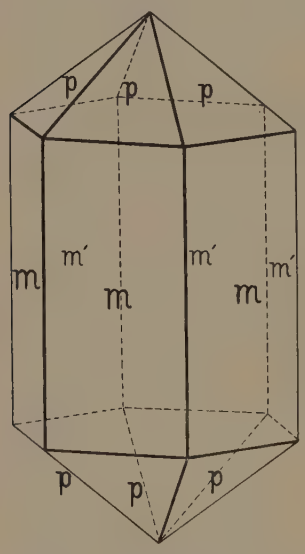


Fig. 2. *Crystalform of* $\{Co(r\text{-}Chxn)_3\}(NO_3)_3 + 3H_2O$

The *chloride, nitrate, chlorate* and *perchlorate* of this series are rather badly soluble in cold, better in hot water; the greater part of the salts dissolved ordinairly falls out on cooling, but sometimes small, well developed crystals can be obtained from the very dilute mother-liquors, by very slow evaporation at room-temperature.

Measurable crystals were, in this way, obtained in the case of the *nitrate*, the *chlorate* and the *perchlorate*.

1. *Tricyclohexanediamine-cobaltic nitrate:* $\{Co(r\text{-}Chxn)_3\}(NO_3)_3 + 3H_2O$ crystallizes in small orange-brown crystals (Fig. 2).

Hexagonal-bipyramidal.

$a:c = 1:0{,}7834$.

Forms observed: $m = \{10\bar{1}0\}$, lustrous and well-developed; $p = \{10\bar{1}1\}$, yields sharp reflections. Short prismatic; no distinct cleavability was observed.

Angular Values:	
$m:m = (10\bar{1}0):(01\bar{1}0) =$	60°
$m:p = (10\bar{1}0):(10\bar{1}1) =$	47° 52′
$p:p = (1\bar{1}01):(10\bar{1}1) =$	39 12
$p:p = (10\bar{1}1):(\bar{1}011) =$	84 16
$m:p = (0\bar{1}10):(1\bar{1}01) =$	70 24

The angles observed and calculated do not differ more than about 4'.

The LAUE-diagram on {001} proved to have *no* planes of symmetry, but the crystals are *not* piezo-electrical. Optically uniaxial, negative; according to Dr. TERPSTRA, for yellow light n_ω is 1,5830, for green (Hg): 1,5863; for yellow light n_ε is: 1,5744, for green light: 1,5783.

The analysis of the *nitrate* gave: 8,03 % H_2O; 19,8 % N; calculated: 8,4 % H_2O; 19,66 % N.

2. *Tricyclohexanediamine-cobaltic chlorate*: $\{Co(r\text{-}Chxn)_3\}(ClO_3)_3$ was also obtained from its solutions in small, prismatic needles, which, according to Dr. TERPSTRA — who was kind enough to study these small individuals by the aid of the theodolite-goniometer — are of *two* different kinds. The one form (α) is *hexagonal* and evidently closely related to the analogously constituted *nitrate* and *perchlorate*; the other kind of crystals (β) is *monoclinic-prismatic*. Neither the chloride nor the nitrate, however, proved to be present in the preparation; whilst the *β-chlorate*, according to its analysis, is *anhydrous*, the *α-chlorate*, like the *nitrate* and *perchlorate*, most probably crystallizes with 3 molecules of water.

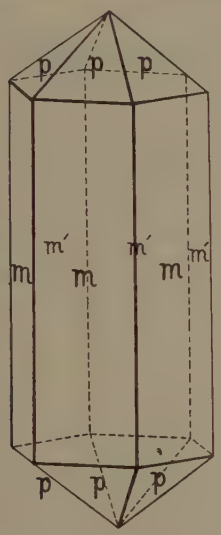


Fig. 3. *Crystalform of* $\alpha\text{-}\{Co\,(r\text{-}Chxn)_3\}\,(ClO_3)_3 + 3H_2O$

The hexagonal-bipyramidal α-form (Fig. 3) has the axial ratio: $a : c = 1 : 0{,}7653$.

Forms observed: $m = \{10\bar{1}0\}$, larger than $p = \{10\bar{1}1\}$, yields bad reflections; the habitus is short-prismatic parallel to the *c*-axis. The analogy with the *nitrate* is seen from a comparison of the angular values:

$$\begin{aligned} m : m &= (10\bar{1}0) : (01\bar{1}0) = 60^\circ \\ m : p &= (10\bar{1}0) : (10\bar{1}\bar{1}) = 48^\circ\ 32' \\ p : p &= (1\bar{1}01) : (10\bar{1}\bar{1}) = 38\ 40 \\ p : p &= (10\bar{1}\bar{1}) : (\bar{1}011) = 82\ 56 \\ m : p &= (0\bar{1}10) : (1\bar{1}01) = 70\ 40 \end{aligned}$$

Optically uniaxial, negative; the index n_ω is greater than 1,566 and smaller than 1,580.

The specific weight of the crystals is: 1,471.

The β-form of the *chlorate* is *monoclinic-prismatic*; the axial ratio is: $a : b : c = 1{,}7282 : 1 : 1{,}5944$, with $\beta = 81^\circ 26\frac{1}{2}'$. (Fig. 4). In this position the *c*-axis appears to have the character of a morphologically pseudo-hexagonal axis of the crystals. The crystals are elongated parallel to the *b*-axis; they manifest the following forms: $a = \{100\}$ and $s = \{101\}$, also

$r = \{\bar{1}01\}$, about equally broad; but the reflections in this zone are rather bad and the angular values appreciably oscillate; $c = \{001\}$, very narrow;

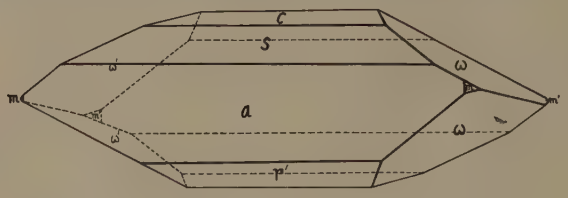


Fig. 4. *Crystalform of* β-$\{Co(r\text{-}Chxn)_3\}(ClO_3)_3$

$\omega = \{112\}$, well developed and yielding good images, like $o = \{\bar{1}11\}$, which, however, is much smaller than ω; $m = \{110\}$, small and like $b = \{010\}$, mostly absent.

Angular Values:	*Observed*:	*Calculated*:
$b : \omega = (010) : (\bar{1}12) =$	*52° 45½′	—
$b : o = (010) : (\bar{1}11) =$	*38 32	—
$a : s = (100) : (101) =$	*42 42½	—
$a : m = (100) : (110) =$	59 41	59° 40′
$c : \omega = (001) : (\bar{1}12) =$	44 21	44 21½
$c : o = (001) : (\bar{1}11) =$	64 39	64 39½
$c : r = (001) : (\bar{1}01) =$	46 36	46 36

No distinct cleavability was observed.

On $\{\bar{1}01\}$ an axial image is visible, with the b-axis as second bisectrix. The plane of the optical axes is perpendicular to $\{010\}$.

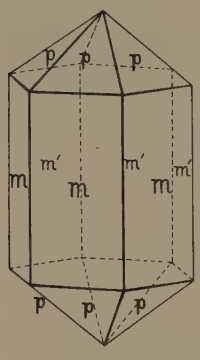


Fig. 5. *Crystalform of* r-$\{Co(Chxn)_3\}(ClO_4)_3 + 3H_2O$

3. The very sparely soluble *perchlorate*: $\{Co(r\text{-}Chxn)_3\}(ClO_4)_3 + 3H_2O$ crystallizes in aggregations of very small, short prismatic crystals. They also are *hexagonal-bipyramidal*, with: $a : c = 1 : 0{,}7644$. The crystals manifest the forms: $m = \{10\bar{1}0\}$ and $p = \{10\bar{1}1\}$ and in their habitus exactly resemble those of the *nitrate*, *chlorate*, etc. (Fig. 5). Also the angular values, measured by means of the theodolite-goniometer, are perfectly analogous to those of the compounds mentioned:

Angular Values:	*Observed*:	*Calculated*:
$m : p = (10\bar{1}0) : (10\bar{1}1) =$	*48° 34′	—
$p : p = (10\bar{1}1) : (01\bar{1}1) =$	70 40	70 40⅔

Optically uniaxial, negative the refractive index $n_\omega = 1{,}563$.
The specific weight of the crystals is: 1,550.

The analysis of the *perchlorate* yielded a water-content of 6,48 %, which is somewhat less than that required: 7,16 % for $3H_2O$.

The remarkable fact that the *α-chlorate*, the *nitrate* and the *perchlorate* have quite analogous crystalforms, — an analogy which borders on isomorphism, — illustrates the predominant influence of the symmetry of the complex ion upon the crystalform. This ion doubtlessly must have a hexagonal or trigonal symmetry and the presence of this senary or trigonal axis appears to be preserved even in some of the optically active salts, such as the *d-* and *l-chlorides*.

§ 4. In the analogous reactions, executed by using the *levo-* or *dextro-*gyratory components of the base, of course, the correspondingly constituted salts of these components are obtained; they will later on be described in detail. First, however, it seems necessary to describe the fission of the *tricyclohexanediamine-cobaltic chloride* into its optically active components, which can be readily performed by means of the *chloro-d-tartrates*. For this purpose a certain quantity of the racemic chloride was treated with the calculated amount of *silver-d-tartrate* and the solution, after removing the precipitate of *AgCl*, subjected to a fractional crystallization. The first, *least* soluble fractions chiefly consist of the pale, orange-yellow *chloro-d-tartrate* of the *levogyratory ion*, the last of the darker coloured, appreciably more soluble *chloro-d-tartrate* of the *dextro*gyratory salt.

In solution they immediately betray their abnormal rotatory dispersion and a COTTON-effect, thus giving proof of the fact, that a fission of the complex ion really has occurred.

The least soluble *chloro-d-tartrate* was proved to have the composition: $L\text{-}\{Co(d\text{-}Chxn)_3\}\begin{matrix}Cl\\(C_4O_6H_4)\end{matrix} + 2H_2O$, with 6,3 % H_2O; calculated: 6,49 % H_2O. Occasionally the water-content of the needles was somewhat less and in better agreement with about 1,5 H_2O. It crystallizes in fine, yellow, prismatic needles, but up till now it could not be obtained in measurable crystals. The *chloro-d-tartrate* of the *dextro*gyratory ion has the composition: $D\text{-}\{Co(l\text{-}Chxn)_3\}\begin{matrix}Cl\\C_4O_6H_4\end{matrix} + 5H_2O$, (with 13,6 % H_2O i.e. somewhat more than $5H_2O$) and (in the anhydrous salt): 6,09 *Cl*.

$D\text{-}\{Co(l\text{-}Chxn)_3\}\begin{matrix}Cl\\(C_4H_4O_6)\end{matrix} + 5H_2O$ forms very small crystals, which were measured in the ordinary way and by means of the theodolite-goniometer by Dr. TERPSTRA. The angular values prove to oscillate strongly: divergencies of 2° are not rare.

The crystals are *rhombic-bisphenoidal*, with $a:b:c = 1{,}668:1:2{,}492$.

Forms observed:

$r = \{101\}$ and $q = \{011\}$, predominant; $m = \{110\}$, very small, but well measurable.

The habitus is variable, but mostly prismatic parallel tot the *b*-axis. (Fig. 6).

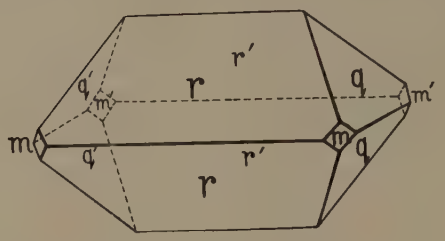


Fig. 6. *Crystalform of* $D\text{-}\left\{Co(l\text{-}Chxn)_3\right\}\left\{\begin{matrix}Cl\\C_4O_6H_4\end{matrix}\right. + H_2O$

Angular Values:	*Observed:*	*Calculated:*
$q:q = (011):(01\bar{1}) =$	*43° 44′	—
$m:m = (110):(\bar{1}10) =$	61 52	—
$r:r = (101):(10\bar{1}) =$	67 44	67° 37′
$m:r = (110):(101) =$	64 45	64 43
$m:q = (110):(011) =$	37 20	37 15

The *c*-axis has a pseudo-hexagonal character.
The crystals are feebly but clearly piezo-electrical.

§ 5. The rotatory dispersion of the two *chloro-d-tartrates* proves to be somewhat variable with the higher or lower concentration of the solution used; but its general character is the same as that of the *chlorides* separated from them and is identical for both series of salts, but for the opposite algebraïc signs. The *least* soluble *chloro-d-tartrate* shows *negative* rotations for wave-lengths greater than about 5890 Å; here the rotation becomes *zero* and then *positive* with a maximum in the vicinity of 5240 Å., subsequently diminishes to *zero* at about 5090 Å., then again becomes strongly *negative,* with a very steep minimum in the neighbourhood of 4730 Å. As will be demonstrated later on, this rotatory dispersion is characteristic of the complex ion containing three molecules of the *dextro*gyratory base. On the other hand, the behaviour of the *most* soluble *chloro-d-tartrate* and of the *chloride* isolated from it is the exact mirror-image of the first, in so far as the algebraïc signs of the rotations are concerned: the curve of the rotatory dispersion of the *chloride* proves, on closer examination, to be the exact mirror-image of that observed with the salt into which three molecules of the *dextro*gyratory base have been introduced.

As an example of the rotatory dispersion observed with the *chloro-d-tartrates*, we here reproduce the results of the measurements of the specific rotations $[\alpha]$ in the case of the *least soluble* fraction, for a solution containing 0,068 % of the (anhydrous) solute:

TABLE I.

λ:	[α]:	λ:	[α]:
		5340	+ 249°.8
6980	− 51°.4	5224	+ 271.8 *M*
6730	− 55.1	5126	+ 117.6
6480	− 58.7	5036	− 198.4*
6262	− 51.4	4950	− 411.4
6074	− 44.1	4861	− 999.0
5893	0	4793	−1116.7
5735	+ 29.4*	4724	−1146.0 *m*
5592	+ 88.2	4658	−1116.7
5463	+191.0	4596	− 911.0
		4537	− 791.6

The typical aspect of the dispersion-curves in the two cases is represented in figure 7.

The fission of the racemic *bromide* occurs in an analogous way and with the same relations of the solubility of the two *bromo-d-tartrates*: the *chlorides* prepared from the corresponding bromides in all respects proved to be identical with those isolated from the least- and more-soluble *chloro-d-tartrates*. The only difference is that these *bromo-d-tartrates* are so sparely soluble that the less soluble one is almost entirely precipitated in the reaction simultaneously with *Ag-bromide*; therefore, it must be isolated by repeatedly extracting the precipitate formed in a SOXLETT-apparatus by means of boiling water. After fractional crystallization of the solution on the water-bath, the last, darker red coloured mother-liquor chiefly contains the more soluble *bromo-d-tartrate*.

As to the dependence of the rotation and the shift of the zero-points on the concentration, it certainly must be attributed to the electrolytic decomposition of these *chloro-* and *bromo-d-tartrates* and the abnormal rotatory behaviour of the tartaric-acid ions in solution.

§ 6. From these *chloro-d-tartrates* the corresponding *chlorides* were set free by means of strong hydrochloric acid and then purified by recrystallization. The curve of the rotatory dispersion had, in each case, almost the same shape as in the figures *A* and *B*, and the absolute values of [α] proved, within the limits of the experimental uncertainties, to be the same as those observed with the chlorides prepared by the direct intro-

duction of the dextro- and levogyratory base respectively into the optically active *praseo-* (violeo-) salts (see Fig. 8). The zero-points of the curves

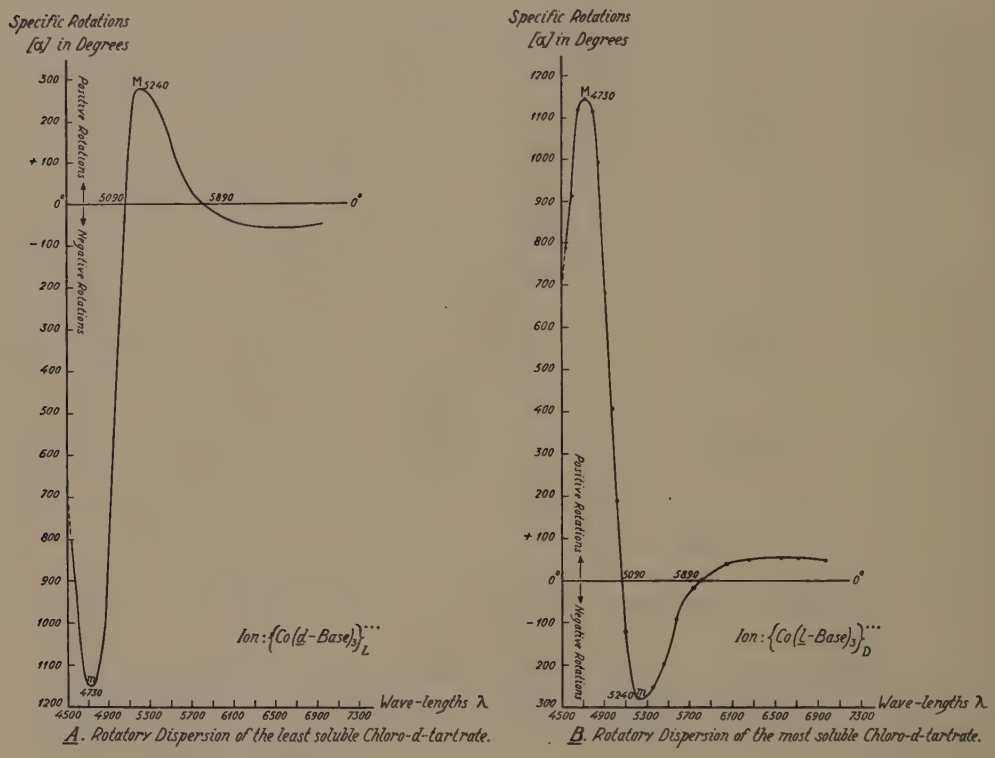


Fig. 7. *Rotatory Dispersion of the two Chloro-d-tartrates of Tricyclohexanediamine-Cobaltic Chloride*

for the pure chlorides appear, to be somewhat shifted towards the greater wave-lengths in comparison with those of the *chloro-d-tartrates.*

§ 7. The preparation of the *praseo*-salt and of the corresponding *tricyclohexanediamine-cobaltic chlorides* now was once more repeated, whilst this time the *optically active components* of the base were used for this purpose. The *praceo*-salts obtained proved, in their general properties, to be perfectly analogous to that of the inactive base: these hygroscopic, somewhat darker green salts, could not be obtained in a completely pure state and were not suited for analysis either. As in the previous case also in these, the formation of about 5—6 % of a black, aromatically smelling, accessory organic compound was observed, which most probably is generated by the oxidation of the base by the hydrogen peroxide used. These optically active *praseo*-salts are, when dissolved in water, also very rapidly transformed into the corresponding *chloro-aquo*, or *diaquo*-salts. Although no quantitative measurements of the rotation of these salts in

aqueous solutions could be made, as a consequence of their strong light-absorption even in small concentrations, it still could be stated that, for instance, the salt $\left\{ \begin{matrix} (l\text{-}Chxn)_2 \\ CoCl \\ H_2O \end{matrix} \right\} Cl_2$ showed a positive rotation in the red part, a negative rotation in the green part of the spectrum and that its rotatory dispersion already possessed a similar character as that observed with the corresponding *tricyclohexanediamine-cobaltic salts*.

These *praseo*-salts were finally transformed into the corresponding *tricyclohexanediamine-cobaltic chlorides* by heating them with one molecule of the levo- and dextrogyratory base respectively.

In this way it could be demonstrated that, on using, for instance, the *levo*gyratory base, a *tri-l-cyclohexanediamine-cobaltic chloride* was obtained, the rotation of which completely corresponded to that obtained by the earlier conversion of the *most soluble chloro-d-tartrate* into its chloride, as was described in the previous experiments. The use of the *dextro*gyratory base, on the other hand, furnished the other antipode; if the algebraic sign of their rotations in the red part of the spectrum is arbitrarily taken as a standard, then the two salts can be represented by the following symbols of the complex ions present in them: $D\text{-}\{Co(l\text{-}Chxn)_3\}^{\cdots}$ and $L\text{-}\{Co(d\text{-}Chxn)_3\}^{\cdots}$. Other combinations of optically active constituents and of each of the optically active ionic configurations than the two mentioned are evidently *not* stable under these circumstances and are generated, amongst all imaginable combinations of this kind, solely by an exclusively *dissymmetrical* synthesis during the process of their formation.

In using the *in*active $(d\text{-} + l\text{-})$ base and subsequently executing the fission of the racemic salt by means of *d-tartaric acid*, we previously obtained no other isomerides than just *the same* two antipodes mentioned: evidently they really represent the stable spatial configurations of these complex ions in the process involved. The observed relations are, therefore, in the present case exactly the same as they previously were stated by us [1]) in the case of the corresponding cobaltic salts of *cyclopentane-1-2-diamine*, where the ions $\{Co(l\text{-}Cptn)_3\}_D^{\cdots}$ and $\{Co(d\text{-}Cptn)_3\}_L^{\cdots}$, amongst all theoretically possible combinations, equally proved to be the *only really stable* ones formed in the reaction.

In this connection the following experiment still is of interest: The salt $\left\{ Co \begin{matrix} (l\text{-}Chxn)_2 \\ Cl_2 \end{matrix} \right\} Cl$ in aquous solution was boiled with one equivalent of the *dextro*gyratory base. The dark-coloured solution was filtered off, during a short time boiled with *norite*, and the filtered, orange-red solution evaporated on the water-bath. First an orange-red salt crystallized in long, brittle needles, which proved to be *ditetragonal* and in solution manifested

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1) F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. Anorg. Chem., **175**, 161 (1928).

no rotatory power. The crystals proved to be those of the *racemic* compound formerly described. From the last mother-liquors a more soluble fraction was obtained, which in solution showed the rotation characteristic of D-$\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$. *No other compounds* than only these two were obtained. A salt of the composition: $\left\{ Co \begin{matrix} (l\text{-}Chxn) \\ (d\text{-}Chxn) \end{matrix} 2 \right\} Cl_3$ was *not* present, but the latter, being *unstable*, is evidently decomposed according to the formula:

$$3\left\{Co \begin{matrix} (l\text{-}Chxn) \\ (d\text{-}Chxn) \end{matrix} 2\right\} Cl_3 =$$

$$= \overbrace{\{Co\,(l\text{-}Chxn)_3\}\,Cl_3 + [\{Co\,(d\text{-}Chxn)_3\}\,Cl_3}^{\text{racemic salt}} + \{Co\,(l\text{-}Chxn)_3\}\,Cl_3\ .$$

Just as in the case of the analogous *cyclopentane*-diamine salt, the salt with *l*- and *d*-molecules of the base simultaneously present within the complex ion *cannot exist* under these circumstances, but is immediately transformed into the salt with 3 molecules of the *levo*-, or of the *dextro*-gyratory base respectively. By special experiments it was proved that the combination of the hexagonal-pyramidal salts: D-$\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$ and L-$\{Co(d\text{-}Chxn)_3\}Cl_3 + 4H_2O$ in equimolecular quantities gave indeed the *ditetragonal racemic* salt $(+ 1H_2O)$. The latter, therefore, is a *combination* of the salts first mentioned. On making the *racemic* base react with an optically *in*active salt, like *cobaltous chloride*, evidently not only the salts generated in the process are those of the D- and L-complexes, *but simultaneously a real fission of the originally optically inactive base into its antipodes is performed*, its optically active components being selectively directed into the D- or L-ions generated. This indeed is a very remarkable way of resolving a racemic substance into its optically active antipodes. The active bases afterwards can be set free from their complex salts by destruction and distillation with *KOH* and sodium formiate, as previously was already demonstrated in the case of the analogous *cyclopentane-diamine* salts.

§ 8. The rotatory dispersion of the two enantimorphous salts is the same, except for the opposite algebraic signs of the rotations measured. Although even in this case some slight dependency of $[\alpha]$ on the concentration still seems to be present, the values measured yet prove to agree sufficiently to enable us to trace the true shape of the dispersion-curve. In the following table the data for the specific and molecular rotations of D-$\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$ are collected:

The molecular rotations of the analogous compounds containing *d-cyclohexanediamine* have the same mean values, but with opposite algebraic signs.

The latter data of the molecular rotations $[M] \,.\, 10^{-2}$ are graphically represented in Figure 8, curve *I*; they, therefore, correspond to the salt

isolated from the least soluble *halogeno-d-tartrates*. From this it appears that there are two wave-lengths: at about 5650 Å. and at 5126 Å. respec-

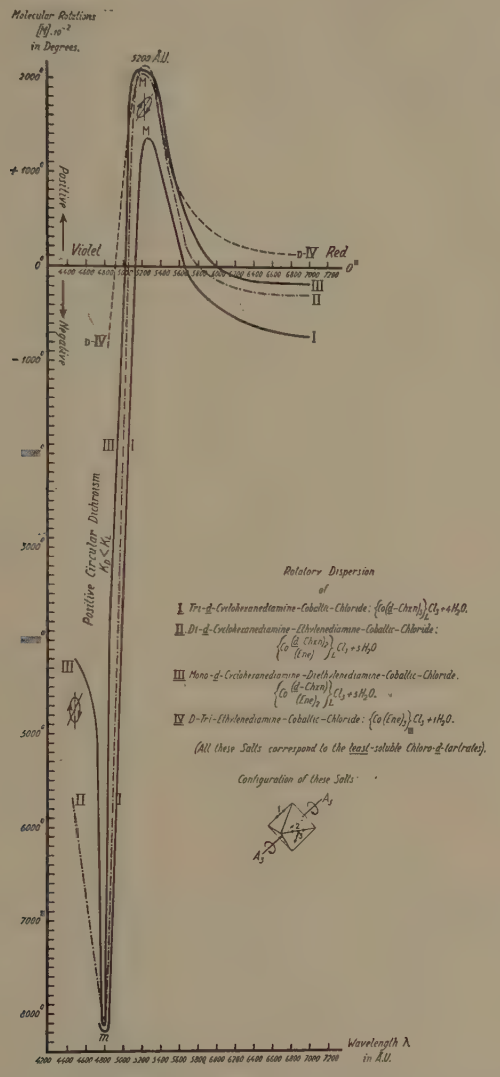

Fig. 8. *Rotatory Dispersion of the Complex Cobaltic Chlorides with 3 molecules of d-Cyclohexanediamine and of those with d-Cyclohexanediamine and 1, 2 and 3 molecules Ethylendiamine respectively.*

tively, — where the rotation of the solutions becomes *zero*; a *maximum* (*minimum* with the other antipode) is present at $\lambda =$ ca. 5300 Å. and a very steep *minimum* (*maximum* with the other antipode) in the vicinity of 4800 Å. Between 4800 and 5300 Å. the absorption-band shows a strong COTTON-effect of positive character.

§ 9. On comparing the molecular rotations with those of the corresponding salts of *cyclopentane-1-2-diamine*, attention must be drawn to the

TABLE II.

Specific and Molecular Rotations of *D*-$\{Co\ (l\text{-Chxn})_3\}Cl_3 + 4\,H_2O$.

Wave-length λ in Å:	Specific Rotation $[\alpha]$ (mean values):	Mean Molecular Rotations $[M] . 10^{-2}$:
6980	125°.6	+ 728°
6730	119.4	+ 692
6480	114.9	+ 666
6262	109.0	+ 632
6074	94.5	+ 548
5893	80.9	+ 469
5735	25.7	+ 149
5592	43.1	— 250
5463	120.6	— 699
5340	221.9	—1286
5224	207.9	—1205
5126	0	0
5036	348.9	+2022
4950	560	+3245
4861	1001	+5801
4793	1428	+8200

fact that the rotations and the dispersion of the latter are in general much greater and are represented by quite another curve, with a minimum (maximum) at about 5000 Å. and a maximum (minimum) at 4430 Å., no wave-lengths of zero-rotation having been found in that case: the *tricyclopentanediamine-cobaltic* salt, corresponding to the *least* soluble *halogeno-d-tartrates*, for instance, there proved to be *levo*gyratory for *all* wave-lengths greater than 4000 A.U. [1]).

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

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[1]) Cf. F. M. JAEGER, these Proceed., **40**, 3, 108 (1937.

Physics. — *La courbe des densités et le diamètre rectiligne du krypton.* Par E. MATHIAS, C. A. CROMMELIN et J. J. MEIHUIZEN. Extrait de la communication N°. 248*b* du laboratoire Kamerlingh Onnes. (Communicated by Prof. W. H. KEESOM.)

(Communicated at the meeting of February 27, 1937).

Les densités du liquide et de la vapeur saturés ont été mesurées à une série de treize températures. On a calculé les ordonnées $y = \frac{1}{2}(\delta_1 + \delta_2)$ du diamètre et on a trouvé que le krypton aussi obéit sensiblement à la loi du diamètre rectiligne.

L'équation du diamètre rectiligne est:

$$y = 1{,}6156 - 0{,}003377\ T,$$

T étant la température en degrés Kelvin, conformément à l'échelle „1936".

Le coefficient angulaire du diamètre est donc

$$\alpha = -0{,}003377.$$

A la température critique 209,39° K le diamètre rectiligne donne pour la densité critique

$$\triangle = 0{,}9085.$$

Le coefficient critique est $K = 3{,}443$.

Mathematics. — *Ueber Produkte von* WHITTAKER*schen Funktionen.* (Zweite Mitteilung) [25]). Von C. S. MEIJER. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of February 27, 1937).

§ 3. Integraldarstellungen für Produkte von parabolischen Zylinderfunktionen.

Aus der Definition (4) der parabolischen Zylinderfunktion geht hervor

$$\left.\begin{aligned} & D_n(z e^{\frac{1}{4}\pi i}) + D_n(z e^{-\frac{1}{4}\pi i}) \\ & = 2^{\frac{1}{2}n+\frac{1}{4}} z^{-\frac{1}{2}} \{e^{-\frac{1}{4}\pi i} W_{\frac{1}{2}n+\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2 e^{\pi i}) + e^{\frac{1}{4}\pi i} W_{\frac{1}{2}n+\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2 e^{-\pi i})\} \\ & = \frac{2^{\frac{1}{2}n+5/4} z^{-\frac{1}{2}} \pi}{\Gamma(\frac{1}{2} - \frac{1}{2}n)} M^*_{-\frac{1}{2}n-\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2), \end{aligned}\right\} \quad . \quad (28)$$

[25]) Erste Mitteilung: Proc. Royal Acad. Amsterdam, **40**, S. 133—141 (1937).

wegen (7) und (2). Auf analoge Weise ergibt sich aus (4), (7) und (2)

$$\left.\begin{aligned} &D_n(z\,e^{\frac{1}{2}\pi i}) - D_n(z\,e^{-\frac{1}{2}\pi i}) \\ &= -\,2^{\frac{1}{2}n+\frac{1}{4}}\,z^{-\frac{1}{2}}\,i\,\{e^{\frac{1}{4}\pi i}\,W_{\frac{1}{2}n+\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2\,e^{\pi i}) + e^{-\frac{1}{4}\pi i}\,W_{\frac{1}{2}n+\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2\,e^{\pi i})\} \\ &= -\,\frac{2^{\frac{1}{2}n+\frac{5}{4}}\,z^{-\frac{1}{2}}\,\pi\,i}{\Gamma(-\frac{1}{2}n)}\,M^*_{-\frac{1}{2}n-\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2). \end{aligned}\right\} \quad . \quad (29)$$

Wegen (4) und (28), bez. (4) und (29), hat man also

$$\left.\begin{aligned} &D_n(z)\,\{D_n(z\,e^{\frac{1}{2}\pi i}) + D_n(z\,e^{-\frac{1}{2}\pi i})\} \\ &\qquad = \frac{2^{n+3/2}\,z^{-1}\,\pi}{\Gamma(\frac{1}{2}-\frac{1}{2}n)}\,W_{\frac{1}{2}n+\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2)\,M^*_{-\frac{1}{2}n-\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2), \end{aligned}\right\} \quad . \quad . \quad (30)$$

bez.

$$\left.\begin{aligned} &D_n(z)\,\{D_n(z\,e^{\frac{1}{2}\pi i}) - D_n(z\,e^{-\frac{1}{2}\pi i})\} \\ &\qquad = -\,\frac{2^{n+3/2}\,z^{-1}\,\pi\,i}{\Gamma(-\frac{1}{2}n)}\,W_{\frac{1}{2}n+\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2)\,M^*_{-\frac{1}{2}n-\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2). \end{aligned}\right\} \quad . \quad . \quad (31)$$

Aus (28) geht hervor

$$\left.\begin{aligned} &\{D_n(z\,e^{\frac{1}{2}\pi i}) + D_n(z\,e^{-\frac{1}{2}\pi i})\}\,\{D_{-n-1}(z\,e^{\frac{1}{2}\pi i}) + D_{-n-1}(z\,e^{-\frac{1}{2}\pi i})\} \\ &\qquad = \frac{4\pi^2\,z^{-1}}{\Gamma(\frac{1}{2}-\frac{1}{2}n)\,\Gamma(1+\frac{1}{2}n)}\,M^*_{-\frac{1}{2}n-\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2)\,M^*_{\frac{1}{2}n+\frac{1}{4},-\frac{1}{4}}(\tfrac{1}{2}z^2); \end{aligned}\right\} \quad . \quad . \quad 32)$$

wegen (29) gilt

$$\left.\begin{aligned} &\{D_n(z\,e^{\frac{1}{2}\pi i}) - D_n(z\,e^{-\frac{1}{2}\pi i})\}\,\{D_{-n-1}(z\,e^{\frac{1}{2}\pi i}) - D_{-n-1}(z\,e^{-\frac{1}{2}\pi i})\} \\ &\qquad = -\,\frac{4\pi^2\,z^{-1}}{\Gamma(-\frac{1}{2}n)\,\Gamma(\frac{1}{2}+\frac{1}{2}n)}\,M^*_{-\frac{1}{2}n-\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2)\,M^*_{\frac{1}{2}n+\frac{1}{4},\frac{1}{4}}(\tfrac{1}{2}z^2). \end{aligned}\right\} \quad . \quad . \quad . \quad (33)$$

Nun hat man [26])

$$K_{\pm\frac{1}{2}}(w) = \sqrt{\frac{\pi}{2w}}\,e^{-w},\; J_{-\frac{1}{2}}(w) = \sqrt{\frac{2}{\pi w}}\cos w,\; J_{\frac{1}{2}}(w) = \sqrt{\frac{2}{\pi w}}\sin w.$$

Ist $|\arg z| < \frac{1}{4}\pi$ und $\Re(n) < 0$, so folgt also aus (30) und (11) (ich setze $v = u\sqrt{2}$ in (11))

$$D_n(z)\,\{D_n(z\,e^{\frac{1}{2}\pi i}) + D_n(z\,e^{-\frac{1}{2}\pi i})\} = \frac{2^{3/2}\sqrt{\pi}}{\Gamma(-n)}\int_0^\infty J_{-n-\frac{1}{2}}(u^2)\,e^{-zu}\cos zu\,du\,;$$

[26]) WATSON, [9], S. 80, Formel (13), S. 55, Formel (6) und S. 54, Formel (3).

in ähnlicher Weise ergibt sich aus (31) und (11), falls $|arg\, z| < \frac{1}{4}\pi$ und $\Re(n) < \frac{1}{2}$ ist,

$$D_n(z)\{D_n(z e^{\frac{1}{2}\pi i}) - D_n(z e^{-\frac{1}{2}\pi i})\} = -\frac{2^{3/2} i \sqrt{\pi}}{\Gamma(-n)} \int_0^\infty J_{-n-\frac{1}{2}}(u^2)\, e^{-zu} \sin zu\, du.$$

Aus (32) und (12) geht hervor, falls $-1 < \Re(n) < 0$ ist,

$$\{D_n(z e^{\frac{1}{2}\pi i}) + D_n(z e^{-\frac{1}{2}\pi i})\}\{D_{-n-1}(z e^{\frac{1}{2}\pi i}) + D_{-n-1}(z e^{-\frac{1}{2}\pi i})\}$$
$$= -\frac{2^{3/2} \sin n\pi}{\pi} \int_0^\infty K_{n+\frac{1}{2}}(\tfrac{1}{2}v^2)(\cosh zv + \cos zv)\, dv.$$

Für $-2 < \Re(n) < 0$ gilt wegen (33) und (12)

$$\{D_n(z e^{\frac{1}{2}\pi i}) - D_n(z e^{-\frac{1}{2}\pi i})\}\{D_{-n-1}(z e^{\frac{1}{2}\pi i}) - D_{-n-1}(z e^{-\frac{1}{2}\pi i})\}$$
$$= \frac{2^{3/2} \sin n\pi}{\pi} \int_0^\infty K_{n+\frac{1}{2}}(\tfrac{1}{2}v^2)(\cosh zv - \cos zv)\, dv.$$

Die Funktion $D_n(z)$ besitzt bekanntlich für $\Re(n) < 0$ die Integraldarstellung [27])

$$D_n(z) = \frac{e^{-\frac{1}{4}z^2}}{\Gamma(-n)} \int_0^\infty u^{-n-1} e^{-zu-\frac{1}{2}u^2}\, du.$$

Ich werde jetzt eine verwandte Integralformel für $D_n(z e^{\frac{1}{2}\pi i})\, D_n(z e^{-\frac{1}{2}\pi i})$ ableiten. Ist $|arg\, z| < \frac{1}{4}\pi$ und $\Re(n) < 0$, so folgt nämlich aus (30), mit Rücksicht auf (18) (mit $k = \frac{1}{2}n + \frac{1}{4}$, $m = -\frac{1}{4}$, $\alpha = \frac{3}{4} - \frac{1}{2}n$, $\beta = -\frac{1}{4} - \frac{1}{2}n$ und $\frac{1}{2}z^2$ statt z angewendet),

$$\left.\begin{aligned}
&D_n(z)\{D_n(z e^{\frac{1}{2}\pi i}) + D_n(z e^{-\frac{1}{2}\pi i})\} = \frac{2^{n+3/2} z^{2n} \pi^{3/2}}{\Gamma(-n)} \int_0^\infty v^{-n-\frac{1}{2}} J_{-n-\frac{1}{2}}(v) \\
&\times \left\{ \frac{1}{\Gamma(\frac{1}{2}+\frac{1}{2}n)\,\Gamma(\frac{1}{2}-\frac{1}{2}n)}\ {}_4F_3\left(\begin{matrix} -\frac{1}{2}n, \frac{1}{4}-\frac{1}{2}n, \frac{1}{2}-\frac{1}{2}n, \frac{3}{4}-\frac{1}{2}n; \\ \frac{1}{2}, -n, \frac{1}{2}-n; \end{matrix} -4v^2/z^4 \right) \right. \\
&\left. + \frac{n-\frac{1}{2}}{\Gamma(\frac{1}{2}n)\,\Gamma(1-\frac{1}{2}n)} \frac{v}{z^2}\ {}_4F_3\left(\begin{matrix} \frac{1}{2}-\frac{1}{2}n, \frac{3}{4}-\frac{1}{2}n, 1-\frac{1}{2}n, \frac{5}{4}-\frac{1}{2}n; \\ \frac{3}{2}, \frac{1}{2}-n, 1-n; \end{matrix} -4v^2/z^4 \right) \right\} dv \\
&= \frac{2^{n+\frac{1}{2}} z^{2n} \sqrt{\pi}}{\Gamma(-n)} \int_0^\infty v^{-n-\frac{1}{2}} J_{-n-\frac{1}{2}}(v) \\
&\times \left\{ e^{\frac{1}{2}n\pi i}\, {}_2F_1\left(\begin{matrix} -n, \frac{1}{2}-n; \\ -2n; \end{matrix} 2iv/z^2 \right) + e^{-\frac{1}{2}n\pi i}\, {}_2F_1\left(\begin{matrix} -n, \frac{1}{2}-n; \\ -2n; \end{matrix} -2iv/z^2 \right) \right\} dv.
\end{aligned}\right\} \quad (34)$$

[27]) Man vergl. WHITTAKER and WATSON, [12], § 16.6 und § 12.22; siehe auch MEIJER, [3], S. 54—57.

Auf analoge Weise ergibt sich aus (31), mit Rücksicht auf (18) (jetzt mit $k=\frac{1}{2}n+\frac{1}{4}$, $m=\frac{1}{4}$, $\alpha=\frac{3}{4}-\frac{1}{2}n$, $\beta=-\frac{1}{4}-\frac{1}{2}n$ und $\frac{1}{2}z^2$ statt z angewendet), falls $|\arg z|<\frac{1}{4}\pi$ und $\Re(n)<0$ ist,

$$\left.\begin{aligned} D_n(z)\{D_n(z\,e^{\frac{1}{2}\pi i})-D_n(z\,e^{-\frac{1}{2}\pi i})\} &= \frac{2^{n+\frac{1}{2}}\,z^{2n}\sqrt{\pi}}{\Gamma(-n)}\int_0^\infty v^{-n-\frac{1}{2}}J_{-n-\frac{1}{2}}(v) \\ \times\left\{e^{\frac{1}{2}n\pi i}\,{}_2F_1\left(\begin{matrix}-n,\,\frac{1}{2}-n;\\ -2n;\,2iv/z^2\end{matrix}\right)-e^{-\frac{1}{2}n\pi i}\,{}_2F_1\left(\begin{matrix}-n,\,\frac{1}{2}-n;\\ -2n;\,-2iv/z^2\end{matrix}\right)\right\}dv. & \end{aligned}\right\}. \quad (35)$$

Durch Addition von (34) und (35) findet man

$$2\,D_n(z)\,D_n(z\,e^{\frac{1}{2}\pi i})=\frac{2^{n+3/2}\,z^{2n}\,e^{\frac{1}{2}n\pi i}\sqrt{\pi}}{\Gamma(-n)}\int_0^\infty v^{-n-\frac{1}{2}}J_{-n-\frac{1}{2}}(v)$$
$$\times\,{}_2F_1\,(-n,\,\tfrac{1}{2}-n;\,-2n;\,2iv/z^2)\,dv.$$

Diese Beziehung gilt (wegen der Theorie der analytischen Fortsetzung) für $-\frac{3}{4}\pi<\arg z<\frac{1}{4}\pi$. Die Funktion $D_n(z\,e^{\frac{1}{4}\pi i})\,D_n(z\,e^{-\frac{1}{4}\pi i})$ besitzt also, falls $|\arg z|<\frac{1}{2}\pi$ und $\Re(n)<0$ ist, die Integraldarstellung

$$\left.\begin{aligned} D_n(z\,e^{\frac{1}{4}\pi i})\,D_n(z\,e^{-\frac{1}{4}\pi i}) &= \frac{2^{n+\frac{1}{2}}\,z^{2n}\sqrt{\pi}}{\Gamma(-n)}\int_0^\infty v^{-n-\frac{1}{2}}J_{-n-\frac{1}{2}}(v) \\ &\times\,{}_2F_1\,(-n,\,\tfrac{1}{2}-n;\,-2n;\,-2v/z^2)\,dv. \end{aligned}\right\}. \quad (36)$$

Nun hat man [28])

$${}_2F_1\,(-n,\,\tfrac{1}{2}-n;\,-2n;\,-y)=\frac{1}{\sqrt{1+y}}\left\{\frac{2\,(\sqrt{1+y}-1)}{y}\right\}^{-2n-1},$$

somit

$$z^{2n}\,{}_2F_1\,(-n,\,\tfrac{1}{2}-n;\,-2n;\,-2v/z^2)=\frac{v^{2n+1}}{\sqrt{z^2+2v}}\,(\sqrt{z^2+2v}-z)^{-2n-1},$$

so dass aus (36) folgt

$$D_n(z\,e^{\frac{1}{4}\pi i})\,D_n(z\,e^{-\frac{1}{4}\pi i})=\frac{2^{n+\frac{1}{2}}\sqrt{\pi}}{\Gamma(-n)}\int_0^\infty v^{n+\frac{1}{2}}J_{-n-\frac{1}{2}}(v)\,(\sqrt{z^2+2v}-z)^{-2n-1}\,\frac{dv}{\sqrt{z^2+2v}}. \quad (37)$$

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[28]) Siehe MEIJER, [3], S. 56.

Setzt man nun

$$\sqrt{z^2+2v}-z=u,$$

also

$$v=zu+\tfrac{1}{2}u^2 \quad \text{und} \quad \frac{dv}{du}=\sqrt{z^2+2v},$$

so bekommt Beziehung (37) die sehr einfache Gestalt

$$D_n(z\,e^{\frac{1}{2}\pi i})\,D_n(z\,e^{-\frac{1}{2}\pi i})=\frac{2^{n+\frac{1}{2}}\sqrt{\pi}}{\Gamma(-n)}\int_L u^{-n-\frac{1}{2}}(z+\tfrac{1}{2}u)^{n+\frac{1}{2}}J_{-n-\frac{1}{2}}(zu+\tfrac{1}{2}u^2)\,du;$$

hierin ist L die die Punkte 0 und $\infty-z$ verbindende Kurve der komplexen u-Ebene, die der positiven reellen Achse der v-Ebene entspricht (ist $z>0$, so ist L die positive reelle Achse der u-Ebene).

Mathematics. — *Eine arithmetische Eigenschaft gewisser ganzer Funktionen.* II. Von J. POPKEN. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of February 27, 1937).

§ 3. *Beweis der Hilfssätze A und B.*

Hier soll zuerst bewiesen werden:

Hilfssatz A: *Zu dem in der Einleitung genannten Operator D und jedem Polynom $G(x)$ gibt es ein und nur ein Polynom $F(x)$ mit*

$$DF(x)=G(x).$$

Zum Operator D und jedem $\nu=0,1,\ldots$ gibt es eine Folge

$$V_{\nu 0}(x),\ V_{\nu 1}(x),\ V_{\nu 2}(x),\ldots$$

von Polynomen, so dass

$$F^{(\nu)}(x)=\sum_{\tau=0}^{\infty} V_{\nu\tau}(x)\,G^{(\tau)}(x)$$

ist; hierbei hat $V_{\nu\tau}(x)$ höchstens den Grad τ und $h^\tau V_{\nu\tau}(x)$ ganze rationale Koeffizienten.

Die natürliche Zahl h ist dabei so gewählt worden, dass die Polynome $h\,P_\nu(x)$ $(\nu=1,2,\ldots,n)$ ganze rationale Koeffizienten haben (siehe § 2).

Hilfssatz 1: *Wird für irgend ein Polynom $G(x)$ die Operation $(1-D)\,G(x)$ durch*

$$(1-D)\,G(x)=G(x)-D\,G(x)=-\sum_{\nu=1}^{n} P_\nu(x)\,G^{(\nu)}(x)$$

definiert, ist ferner

$$(1-D)^0\,G(x)=G(x),\ (1-D)^\tau\,G(x)=(1-D)\,((1-D)^{\tau-1}\,G(x))\ (\tau=1,2,\ldots),$$

so ist $(1-D)^\tau\,G(x)$ für hinreichend grosses τ identisch gleich Null, und

$$F(x)=\sum_{\tau=0}^{\infty}(1-D)^\tau\,G(x)$$

stellt ein Polynom dar mit der Eigenschaft

$$D\,F(x)=G(x).$$

$F(x)$ ist das einzige Polynom, das dieser Differentialgleichung genügt.

Bemerkung: *Aus Hilfssatz 1 folgt also der erste Teil des Hilfssatzes A.*

Beweis: Jedes Polynom $P_\nu(x)$ aus der Differentialgleichung $Df(x)=0$ ist höchstens vom $(\nu-1)$-ten Grade. Für jedes Polynom $R(x)$ vom Grade g ist also $(1-D)\,R(x)=-\sum_{\nu=1}^{n} P_\nu(x)\,R^{(\nu)}(x)$ identisch gleich Null oder höchstens vom Grade $g-1$. Die Gradzahlen der Polynome

$$G(x),\ (1-D)\,G(x),\ (1-D)^2\,G(x),\ldots$$

nehmen also monoton ab bis zuletzt die Polynome der Folge identisch verschwinden. Daher stellt

$$F(x)=\sum_{\tau=0}^{\infty}(1-D)^\tau\,G(x)$$

ein Polynom in x dar

Die Operation $(1-D)$ ist additiv; folglich

$$(1-D)\,F(x)=\sum_{\tau=0}^{\infty}(1-D)^{\tau+1}\,G(x)=F(x)-G(x$$

somit

$$D\,F(x)=G(x).$$

Wäre $F_1(x)$ ein weiteres Polynom mit

$$D\,F_1(x)=G(x),$$

so wäre

$$D(F(x)-F_1(x))=0;$$

nach einer Bemerkung in der Einleitung lässt aber die Differentialgleichung $Df(x) = 0$ kein Polynom $\not\equiv 0$ als Integral zu, also wäre

$$F(x) - F_1(x) \equiv 0.$$

Hiermit ist Hilfssatz 1 bewiesen.

Hilfssatz 2: *Zu dem in der Einleitung genannten Operator D gibt es eine Folge*

$$V_0(x) \equiv 1,\ V_1(x),\ V_2(x), \ldots$$

von Polynomen $V_\tau(x)$ höchstens vom Grade $\tau - 1$ ($\tau = 1, 2, \ldots$), so dass für jedes Polynom $G(x)$

$$F(x) = \sum_{\tau=0}^{\infty} V_\tau(x)\, G^{(\tau)}(x)$$

das nach Hilfssatz 1 eindeutig bestimmte Polynom mit $DF(x) = G(x)$ ist.

Bemerkung: *$F(x)$ hat also genau denselben Grad wie $G(x)$.*

Beweis: Setzt man $V_\tau(x) \equiv 0$ für $\tau < 0$ und $V_0(x) \equiv 1$, so sind nach Hilfssatz 1 mit

$$H_\tau(x) = -\sum_{\nu=1}^{n} P_\nu(x) \sum_{\mu=1}^{\nu} \binom{\nu}{\mu} V_{\tau-\mu}^{(\nu-\mu)}(x) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

statt $G(x)$ angewandt, die Polynome $V_\tau(x)$ eindeutig bestimmt durch die Forderungen

$$D\,V_\tau(x) = H_\tau(x) \qquad (\tau = 1, 2, \ldots) \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

und gilt

$$V_\tau(x) = \sum_{\varkappa=0}^{\infty} (1 - D)^\varkappa\, H_\tau(x).$$

Durch Schluss von τ auf $\tau + 1$ werde ich jetzt zeigen, dass jedes $V_\tau(x)$ ein Polynom höchstens vom Grade $\tau - 1$ ist ($\tau = 1, 2, \ldots$). Für $\tau = 1$ ist

$$H_1(x) = -P_1(x) = -P_1$$

eine Konstante, also $V_1(x) = -P_1$, so dass die Behauptung in diesem Fall evident ist. Man kann daher annehmen, dass $\tau > 1$ und die Behauptung für $V_1(x), V_2(x), \ldots, V_{\tau-1}(x)$ statt $V_\tau(x)$ schon gezeigt worden ist. Dann ist aber $H_\tau(x)$ nach (15) ein Polynom von einem Grade

$$\leqq \operatorname*{Max}_{\substack{\nu=1,2,\ldots,n \\ \mu=1,2,\ldots,\nu}} ((\nu - 1) + (\tau - \mu) - (\nu - \mu)) = \tau - 1,$$

also ist

$$(1 - D)\, H_\tau(x) = -\sum_{\nu=1}^{n} P_\nu(x)\, H_\tau^{(\nu)}(x)$$

ein Polynom von einem Grade $\leqq \tau-2$, $(1-D)^2 H_\tau(x)$ ein Polynom von einem Grade $\leqq \tau-3$, u.s.w., so dass

$$V_\tau(x) = \sum_{\varkappa=0}^{\infty} (1-D)^\varkappa H_\tau(x)$$

tatsächlich ein Polynom höchstens vom Grade $\tau-1$ ist.

Jetzt werde ich zeigen, dass das Polynom

$$F(x) = \sum_{\tau=0}^{\infty} V_\tau(x)\, G^{(\tau)}(x)$$

der Differentialgleichung $DF(x) = G(x)$ genügt. Für $\nu = 1, 2, \ldots$ gilt nämlich

$$\left.\begin{aligned} F^{(\nu)}(x) &= \sum_{\tau=0}^{\infty} \frac{d^\nu}{dx^\nu}\left(V_\tau(x)\, G^{(\tau)}(x)\right) = \sum_{\tau=0}^{\infty} \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} V_\tau^{(\nu-\mu)}(x)\, G^{(\tau+\mu)}(x) \\ &= \sum_{\tau=0}^{\infty} G^{(\tau)}(x) \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} V_{\tau-\mu}^{(\nu-\mu)}(x) = \sum_{\tau=1}^{\infty} G^{(\tau)}(x) \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} V_{\tau-\mu}^{(\nu-\mu)}(x), \end{aligned}\right\} \quad . . (17)$$

wegen $V_0^{(\nu)}(x) = 0$. Daher ist

$$\begin{aligned} DF(x) &= F(x) + \sum_{\nu=1}^{n} P_\nu(x) F^{(\nu)}(x) = F(x) + \sum_{\tau=1}^{\infty} G^{(\tau)}(x) \sum_{\nu=1}^{n} P_\nu(x) \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} V_{\tau-\mu}^{(\nu-\mu)}(x) \\ &= F(x) + \sum_{\tau=1}^{\infty} G^{(\tau)}(x) \left(\sum_{\nu=1}^{n} P_\nu(x)\, V_\tau^{(\nu)}(x) - H_\tau(x) \right), \end{aligned}$$

wegen (15), sodass aus (16) folgt

$$\begin{aligned} DF(x) &= F(x) + \sum_{\tau=1}^{\infty} G^{(\tau)}(x) \left(D V_\tau(x) - V_\tau(x) - D V_\tau(x)\right) \\ &= F(x) - \sum_{\tau=1}^{\infty} V_\tau(x)\, G^{(\tau)}(x) = G(x). \end{aligned}$$

Hilfssatz **2** ist somit bewiesen.

Hilfssatz 3: *Zum Operator D und zu jedem $\nu = 0, 1, \ldots$ gibt es eine Folge*

$$V_{\nu 0}(x),\ V_{\nu 1}(x),\ V_{\nu 2}(x), \ldots$$

von Polynomen, bezw. höchstens von den Graden 0, 1, 2, ... mit folgender Eigenschaft: Ist $G(x)$ ein Polynom und $F(x)$ das nach Hilfssatz 1 eindeutig bestimmte Polynom mit $DF(x) = G(x)$, so gilt

$$F^{(\nu)}(x) = \sum_{\tau=0}^{\infty} V_{\nu\tau}(x)\, G^{(\tau)}(x).$$

Ferner ist

$$V_{\nu\tau}(x) \equiv 0 \text{ für } \tau < \nu,\ V_{\nu\nu}(x) \equiv 1.$$

Bemerkung: *Wird nachher noch gezeigt, dass jedes* $h^\tau V_{\nu\tau}(x)$ *ganze rationale Koeffizienten hat, so ist hiermit auch der zweite Teil von Hilfssatz A bewiesen.*

Beweis: Nach vorigem Hilfssatz ist

$$F(x) = \sum_{\tau=0}^{\infty} V_\tau(x)\, G^{(\tau)}(x),$$

wo $V_0(x) \equiv 1$ und $V_\tau(x)$ Polynome höchstens vom Grade $\tau-1$ sind $(\tau = 1, 2, \ldots)$.

Wird wieder $V_\tau(x) \equiv 0$ für $\tau < 0$ gesetzt, so folgt analog (17) für $\nu = 0, 1, \ldots$

$$F^{(\nu)}(x) = \sum_{\tau=0}^{\infty} G^{(\tau)}(x) \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} V_{\tau-\mu}^{(\nu-\mu)}(x);$$

setzt man

$$\binom{\nu}{\mu} V_{\tau-\mu}^{(\nu-\mu)}(x) = V_{\nu\tau}(x) \sum_{\mu=0}^{\nu} \qquad (\tau = 0, 1, \ldots),$$

so gilt

$$F^{(\nu)}(x) = \sum_{\tau=0}^{\infty} V_{\nu\tau}(x)\, G^{(\tau)}(x),$$

wo $V_{\nu\tau}(x)$ tatsächlich ein Polynom höchstens vom Grade τ ist.

Beachtet man, dass $V_\tau(x) \equiv 0$ für $\tau < 0$, $V_0(x) \equiv 1$ und sonst $V_\tau(x)$ ein Polynom höchstens vom Grade $\tau-1$ ist, so folgt aus der Definition von $V_{\nu\tau}(x)$

$$V_{\nu\tau}(x) \equiv 0 \text{ für } \tau < \nu, \quad V_{\nu\nu}(x) = V_0(x) \equiv 1.$$

Hilfssatz 3 ist also bewiesen.

Hilfssatz 4: *Sei* ν *eine ganze Zahl* $\geqq 0$, *seien* $V_{\nu\tau}(x)$ $(\tau = 0, 1, \ldots)$ *die Polynome aus vorigem Hilfssatz, sei* $V_{\nu\tau}(x) \equiv 0$ *für* $\tau < 0$, *so gilt für jedes ganze* $\tau \geqq \nu + 1$

$$\sum_{\mu=0}^{n} V_{\nu,\tau-\mu}(x) \sum_{\lambda=0}^{n-\mu} \binom{\tau-\mu}{\lambda} P_{\mu+\lambda}^{(\lambda)}(x) = 0, \quad \ldots \quad (18)$$

wo $P_0(x) \equiv 1$ *gesetzt worden ist.*

Beweis: Sei α beliebig, ϱ eine natürliche Zahl und

$$F(x) = 1 + \frac{\alpha x}{1!} + \ldots + \frac{\alpha^\varrho x^\varrho}{\varrho!}.$$

Dann ist

$$F'(x) = \alpha\left(1 + \frac{\alpha x}{1!} + \ldots + \frac{\alpha^{\varrho-1} x^{\varrho-1}}{(\varrho-1)!}\right) = \alpha F(x) - \frac{\alpha^{\varrho+1} x^\varrho}{\varrho!},$$

und allgemeiner

$$F^{(\varkappa)}(x) = \alpha^{\varkappa} F(x) + \alpha^{\varrho+1} Q_{\varkappa}(\alpha, x) \qquad (\varkappa = 0, 1, \ldots), \quad . \quad . \quad (19)$$

wo $Q_{\varkappa}(\alpha, x)$ ein Polynom in α und x darstellt.

Man setze ferner

$$G(x) = DF(x) = \sum_{\nu=0}^{n} P_{\nu}(x) F^{(\nu)}(x);$$

dann gilt für $\sigma = 0, 1, \ldots$

$$G^{(\sigma)}(x) = \sum_{\nu=0}^{n} \sum_{\varkappa=\sigma-\nu}^{\sigma} \binom{\sigma}{\sigma-\varkappa} P_{\nu}^{(\sigma-\varkappa)}(x) F^{(\nu+\varkappa)}(x)$$

$$= \sum_{\mu=0}^{n} F^{(\sigma+\mu)}(x) \sum_{\nu=\mu}^{n} \binom{\sigma}{\nu-\mu} P_{\nu}^{(\nu-\mu)}(x)$$

$$= \sum_{\mu=0}^{n} F^{(\sigma+\mu)}(x) \sum_{\lambda=0}^{n-\mu} \binom{\sigma}{\lambda} P_{\mu+\lambda}^{(\lambda)}(x).$$

Wegen (19) ist daher

$$G^{(\sigma)}(x) = \sum_{\mu=0}^{n} \alpha^{\sigma+\mu} F(x) \sum_{\lambda=0}^{n-\mu} \binom{\sigma}{\lambda} P_{\mu+\lambda}^{(\lambda)}(x) + \alpha^{\varrho+1} R_{\sigma}(\alpha, x), \quad . \quad . \quad (20)$$

wo $R_{\sigma}(\alpha, x)$ ebenfalls ein Polynom in α und x bezeichnet.

Wegen $DF(x) = G(x)$ ist nach Hilfssatz 3

$$F^{(\nu)}(x) = \sum_{\sigma=0}^{\infty} V_{\nu\sigma}(x) G^{(\sigma)}(x),$$

wo die Summe rechterhand nach endlich vielen Summanden abbricht; also nach (19) und (20)

$$\alpha^{\nu} F(x) = \sum_{\sigma=0}^{\infty} V_{\nu\sigma}(x) \sum_{\mu=0}^{n} \alpha^{\sigma+\mu} F(x) \sum_{\lambda=0}^{n-\mu} \binom{\sigma}{\lambda} P_{\mu+\lambda}^{(\lambda)}(x) + \alpha^{\varrho+1} S(\alpha, x),$$

wo $S(\alpha, x)$ ein Polynom in α und x bedeutet, so dass offenbar $\alpha^{\varrho+1} S(\alpha, x)$ durch $F(x)$ teilbar ist. Division durch $F(x) = 1 + \frac{\alpha x}{1!} + \ldots + \frac{\alpha^{\varrho} x^{\varrho}}{\varrho!}$ ergibt

$$\alpha^{\nu} = \sum_{\sigma=0}^{\infty} V_{\nu\sigma}(x) \sum_{\mu=0}^{n} \alpha^{\sigma+\mu} \sum_{\lambda=0}^{n-\mu} \binom{\sigma}{\lambda} P_{\mu+\lambda}^{(\lambda)}(x) + \alpha^{\varrho+1} T(\alpha, x),$$

wo $T(\alpha, x)$ wieder ein Polynom in α und x ist.

Sei τ eine ganze Zahl $\geqq \nu+1$. Man wähle jetzt $\varrho \geqq \tau$; die Koeffizienten von α^τ links und rechts in obenstehender Identität müssen übereinstimmen; wegen $\nu < \tau < \varrho+1$ ist daher

$$0 = \sum_{\mu=0}^{n} V_{\nu,\tau-\mu}(x) \sum_{\lambda=0}^{n-\mu} \binom{\tau-\mu}{\lambda} P_{\mu+\lambda}^{(\lambda)}(x),$$

so dass Hilfssatz 4 gültig ist.

Der Koeffizient von $V_{\nu\tau}(x)$ in (18) ist gleich $P_0(x) = 1$, also

$$-h^\tau V_{\nu\tau}(x) = \sum_{\mu=1}^{n} h^{\tau-1} V_{\nu,\tau-\mu}(x) \sum_{\lambda=0}^{n-\mu} \binom{\tau-\mu}{\lambda} h P_{\mu+\lambda}^{(\lambda)}(x) \qquad (\tau \geqq \nu+1).$$

Beachtet man, dass nach Definition von h die Polynome $h P_\nu(x)$ $(\nu = 1, 2, \ldots, n)$ ganze rationale Koeffizienten haben; ferner, dass mit Rücksicht auf Hilfssatz 3 gilt: $V_{\nu\tau}(x) \equiv 0$ für $\tau < \nu$, $V_{\nu\nu}(x) \equiv 1$, so folgt durch Schluss von τ auf $\tau+1$, dass jedes $h^\tau V_{\nu\tau}(x)$ $(\tau = 0, 1, \ldots)$ ganze rationale Koeffizienten hat. Nach der Bemerkung zu Hilfssatz 3 ist also Hilfssatz A vollständig bewiesen.

Hilfssatz 4 liefert uns aber auch:

Hilfssatz B: *Sei x_0 rational, m eine natürliche Zahl, so dass $m x_0$ ganz ist, seien $a_0, a_1, \ldots, a_{n-1}$ ganze rationale Zahlen, die nicht alle verschwinden, so sind $(mh)^n P_n(x_0)$ und*

$$W_\tau = (mh)^\tau \sum_{\nu=0}^{n-1} a_\nu V_{\nu\tau}(x_0) \qquad (\tau = 0, 1, \ldots)$$

ganz rational.

Ist p eine Primzahl $> m$, $> h$ und $> |a_\nu|$ $(\nu = 0, 1, \ldots, n-1)$, teilt p die Zahl $(mh)^n P_n(x_0)$ nicht, so sind für $\tau > n$ die n Zahlen

$$W_{\tau-1}, \; W_{\tau-2}, \ldots, \; W_{\tau-n}$$

nicht sämmtlich durch p teilbar.

Beweis: Es ist $m x_0$ ganz rational, $h P_n(x)$ ein Polynom mit ganzen rationalen Koeffizienten vom Grade $n-1$, $n \geqq 1$; daher ist $(mh)^n P_n(x_0)$ offenbar ganz rational. Ferner ist $h^\tau V_{\nu\tau}(x)$ nach Hilfssatz A ein Polynom mit ganzen rationalen Koeffizienten höchstens vom Grade τ, daher ist auch jedes $(mh)^\tau V_{\nu\tau}(x_0)$ und somit

$$W_\tau = \sum_{\nu=0}^{n-1} a_\nu (mh)^\tau V_{\nu\tau}(x_0)$$

ganz rational.

Um den zweiten Teil von Hilfssatz B zu beweisen, nehme ich an,

dass für gewisses ganzes $\tau > n-1$ die n Zahlen $W_\tau, W_{\tau-1}, \ldots, W_{\tau-n+1}$ alle durch p teilbar sind. Diese Annahme wird zu einem Widerspruch führen. In Formel (18) aus Hilfssatz 4 ist nämlich der Koeffizient von $V_{\nu,\tau-n}(x)$ gleich $P_n(x)$, also folgt für jedes ganze $\tau > \nu$

$$-(m\,h)^n P_n(x_0) \,.\, (m\,h)^{\tau-n} V_{\nu,\tau-n}(x_0) =$$

$$\sum_{\mu=0}^{n-1} (m\,h)^{\tau-\mu} V_{\nu,\tau-\mu}(x_0) \sum_{\lambda=0}^{n-\mu} \binom{\tau-\mu}{\lambda} (m\,h)^\mu P_{\mu+\lambda}^{(\lambda)}(x_0),$$

also gilt wegen

$$W_\tau = \sum_{\nu=0}^{n-1} a_\nu (m\,h)^\tau V_{\nu\tau}(x_0) \qquad (\tau = 0, 1, \ldots)$$

für $\tau > n-1$

$$-(m\,h)^n P_n(x_0)\, W_{\tau-n} = \sum_{\mu=0}^{n-1} W_{\tau-\mu} \sum_{\lambda=0}^{n-\mu} \binom{\tau-\mu}{\lambda} (m\,h)^\mu P_{\mu+\lambda}^{(\lambda)}(x_0).$$

Hierin ist jede Zahl $(m\,h)^\mu P_{\mu+\lambda}^{(\lambda)}(x_0)$ ganz rational; denn für $\mu = \lambda = 0$ ist $P_{\mu+\lambda}^{(\lambda)}(x) \equiv 1$, für $\mu = 0$, $\lambda > 0$ ist $P_{\mu+\lambda}^{(\lambda)}(x) \equiv 0$ und für $\mu > 0$ ist $h^\mu P_{\mu+\lambda}^{(\lambda)}(x)$ ein Polynom mit ganzen rationalen Koeffizienten höchstens vom Grade $\mu-1$.

Wäre nun p Teiler von $W_\tau, W_{\tau-1}, \ldots, W_{\tau-n+1}$, so wäre nach voriger Beziehung p auch Teiler von $(m\,h)^n P_n(x_0)\, W_{\tau-n}$, und, da p die Zahl $(m\,h)^n P_n(x_0)$ nach Voraussetzung nicht teilt, wäre p sogar Teiler von $W_{\tau-n}$. Wiederholung dieser Schlussweise ergibt, dass p Teiler aller Zahlen $W_\tau, W_{\tau-1}, \ldots, W_0$ sein würde. Insbesondere wäre p Primteiler von W_t, wo t so gewählt wird, dass a_t die erste nichtverschwindende Zahl in der Folge $a_0, a_1, \ldots, a_{n-1}$ ist, so dass

$$\begin{aligned} W_t &= (m\,h)^t (a_t V_{tt}(x_0) + a_{t+1} V_{t+1,t}(x_0) + \ldots + a_{n-1} V_{n-1,t}(x_0)) \\ &= (m\,h)^t a_t, \end{aligned}$$

wegen Hilfssatz 3, ist. Mindestens eine der Zahlen m, h, a_t wäre also durch p teilbar, was $p > m$, $> h$, $> |a_t|$ widerspricht.

Für $\tau > n-1$ sind also die n Zahlen $W_\tau, W_{\tau-1}, \ldots, W_{\tau-n+1}$ nicht sämmtlich durch p teilbar, und Hilfssatz B ist bewiesen.

Mathematics. — *Note on linear operators.* By CORNELIS VISSER. (Communicated by Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of February 27, 1937).

1. We consider a HILBERT space $\mathfrak{H}$. The following theorem is due to F. RIESZ [1]).

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[1]) F. RIESZ, Ueber die linearen Transformationen des komplexen Hilbertschen Raumes, Acta litt. ac. scient., Szeged, **5**, 23—54 (1930).

Theorem. Any bounded self-adjoint operator A in $\mathfrak{H}$ can be expressed in the form

$$A = R - S,$$

where R and S are two positive definite bounded self-adjoint operators which satisfy the relation

$$RS = 0$$

and which are permutable with every bounded linear operator which is permutable with A. This decomposition is unique.

In RIESZ's formulation the theorem states a little more: R and S are of the form $R = AP$, $S = -AQ$, where P and Q are two projections which satisfy the relation $P + Q = I$ (= identity) and which are permutable with every bounded linear operator which is permutable with A. This, however, is easily established once the theorem in the above form has been demonstrated.

In the present note I shall give an elementary proof of RIESZ's theorem. It is based upon the same idea as a proof given by WECKEN [2]), but is carried out in a different way. My tools will be well-known facts about the limit of a bounded non-decreasing sequence of self-adjoint operators and further the fact that the product of two permutable positive definite bounded self-adjoint operators is again positive definite. For this I refer to RIESZ's paper.

2. We start with the following

Lemma. If A and B are bounded self-adjoint operators for which

$$A + B \geqq 0 \text{ and } AB = 0,$$

then

$$A \geqq 0 \text{ and } B \geqq 0.$$

Proof. Let P denote the projection on the closed linear manifold formed by all elements x in $\mathfrak{H}$ for which $Ax = 0$. The relation $AB = 0$ implies $PB = B$. We have further $AP = 0$; hence $PA = 0$. Therefore

$$0 \leqq P(A + B) = PA + PB = PB = B.$$

In a similar way, using the fact that $AB = 0$ implies $BA = 0$, we find $A \geqq 0$.

3. Proceeding to the proof of the theorem, we put

$$B_0 = 0,$$
$$B_{n+1} = B_n + \tfrac{1}{2}(A^2 - B_n^2) \qquad (n = 0, 1, 2, \ldots)$$

With the help of the relations

$$I - B_{n+1} = \tfrac{1}{2}(I - B_n)^2 + \tfrac{1}{2}(I - A^2)$$
$$2(B_{n+1} - B_n) = (I - B_{n-1})^2 - (I - B_n)^2,$$

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[2]) F. J. WECKEN, Zur Theorie linearer Operatoren, Math. Ann. **110**, 722—725 (1934).

mathematical induction shows that

$$0 \leqq B_n \leqq B_{n+1} \leqq I.$$

Consequently the sequence B_n has a limit B, which is a positive definite bounded self-adjoint operator. Since every B_n is permutable with any bounded linear operator which is permutable with A, B has the same property. Obviously B satisfies the relation

$$B = B + \tfrac{1}{2}(A^2 - B^2);$$

hence

$$B^2 = A^2.$$

We now put

$$R = \tfrac{1}{2}(B + A), \qquad S = \tfrac{1}{2}(B - A).$$

Then $R + S = B \geqq 0$ and $RS = 0$. Hence, by virtue of the lemma, $R \geqq 0$ and $S \geqq 0$. Further $A = R - S$ and finally we observe that R and S have the required permutability property, because B has.

Thus the existence of R and S has been proved. We next show their unicity. Suppose that we had a second decomposition $A = R_1 - S_1$ with the same properties. Then

$$(R - R_1) - (S - S_1) = 0.$$

Squaring yields

$$(R - R_1)^2 + (S - S_1)^2 + 2RS_1 + 2R_1S - 2RS - 2R_1S_1 = 0.$$

Since $RS = R_1S_1 = 0$, $R_1S \geqq 0$, $RS_1 \geqq 0$, all members on the left must vanish. In particular

$$(R - R_1)^2 = (S - S_1)^2 = 0;$$

hence $R = R_1$ and $S = S_1$.

4. Finally we show how the form in which RIESZ expresses the theorem may be obtained. Let P denote the projection on the closed linear manifold formed by all x for which $Sx = 0$. P is permutable with every bounded linear operator which is permutable with A. For, if L is such an operator, $0 = LAP = ALP$, whence $PLP = LP$. Likewise $PL^*P = L^*P$, where L^* is the adjoint of L. On taking adjoints, we obtain $PLP = PL$. Hence $LP = PL$.

The relation $SR = 0$ implies $PR = RP = R$. Hence $AP = (R - S)P = RP - SP = RP = R$ and, if we put $Q = I - P$, $-AQ = -A + R = S$. Thus RIESZ's theorem has been proved to its full extent.

Plantkunde. — *De periodiciteit der bloemvorming bij Calluna vulgaris (L.) Hull.* Door W. BEIJERINCK. (Mededeeling N°. 14 van het Biologisch Station te Wijster). (Aangeboden door Prof. A. H. BLAAUW).

(Communicated at the meeting of February 27, 1937).

Calluna overwintert met open bladknoppen. De jongste blaadjes zijn naar elkaar toe gebogen over het terminaal gelegen hoofd-vegetatiepunt en beschermen dit, mede door de aan de bladtoppen zich bevindende trichomen, tegen vocht en andere storende invloeden van buitenaf.

Behalve dit terminaal gelegen groeipunt bevinden zich dikwijls nog laterale groeipunten aan het dichtbebladerde kortlot, n.l. in de oksels der dakpansgewijs over elkaar gelegen, decussaat geplaatste, kort naaldvormige blaadjes (Fig. 2 en 3).

In het vroege voorjaar, soms reeds in Februari, zoodra het weer en de overige omstandigheden het toelaten, heeft op onze breedte een strekking plaats van de knop-internodiën en jonge blaadjes, terwijl deelingen in het meristeem der groeipunten plaats vinden, waardoor nieuwe blad-primordia worden afgesnoerd. Deze eerste strekkingsperiode heeft echter met „horten en stooten" plaats, al naar gelang de weersomstandigheden dit medebrengen.

Uit de laterale vegetatiepunten kunnen, evenals uit de terminale, langloten of kortloten voortkomen, die op hun beurt in het zelfde groeiseizoen zich kunnen vertakken, zijscheuten vormend van de eerste, tweede en bij hooge uitzondering zelfs van de derde orde. Ook komen overgangen voor tusschen lang- en kortloten of kan periodiek een langlot als kortlot verder groeien, — zooals dit geregeld gebeurt in den herfst, — of omgekeerd, een kortlot groeit als langlot verder, zooals dit in het voorjaar geregeld voorkomt.

Tegen den winter wordt zoowel de internodiën-lengte als de bladlengte gereduceerd, zoo dat de dicht opeengepakte en apicaal kleiner wordende, overblijvende loofbladen in het volgend groeiseizoen de plaats aanduiden, waar de winterknop heeft gelegen. De kortlotbladen kunnen 2—2½ jaar groen blijven, in tegenstelling met de doorgaans binnen het groeiseizoen afstervende langlotbladen, in wier oksel de zijscheuten ontspringen. Bij uitzondering kunnen aan krachtig ontwikkelde planten de langlotbladen levend overwinteren om dan in het volgende voorjaar af te sterven.

Calluna vormt dus rijk vertakte jaarscheuten. Beziet men nu gedurende den bloeitijd in Augustus of September een krachtig ontwikkelden jaarscheut, welke meestal 15—20 cm, bij uitzondering 50—55 cm lengte bereikt, dan kunnen daaraan drie zônes worden onderscheiden, n.l.:

1e, een basaal gedeelte met uitsluitend assimilatie-loten van de 1e, 2e en zelden van de 3e orde;
2e, een middengedeelte met zoowel bladen als bloemen dragende zijloten van de 1e, 2e en bij uitzondering van de 3e orde;
3e, een apicaal gedeelte met wederom uitsluitend assimilatie-loten, dus zonder bloemen.

De bloemen staan steeds terminaal aan bebladerde kortloten of aan daarmede gelijk te stellen, uitsluitend van 2 prophyllen en eenige bracteeënparen voorziene bloemtwijgjes. De vrij regelmatige rangschikking der bloemen aan dergelijke korte zijloten langs den zeer veel langeren jaarscheut kan, oppervlakkig bekeken, den indruk maken van een bloemtros, maar is in wezen slechts een schijntros of trosvormige rangschikking van terminale, alleen staande bloemen. Immers, het apicale gedeelte van den jaarscheut groeit verder en vormt in het volgende groeiseizoen, uit de daar aanwezige kortloten, doorgaans meerdere langloten.

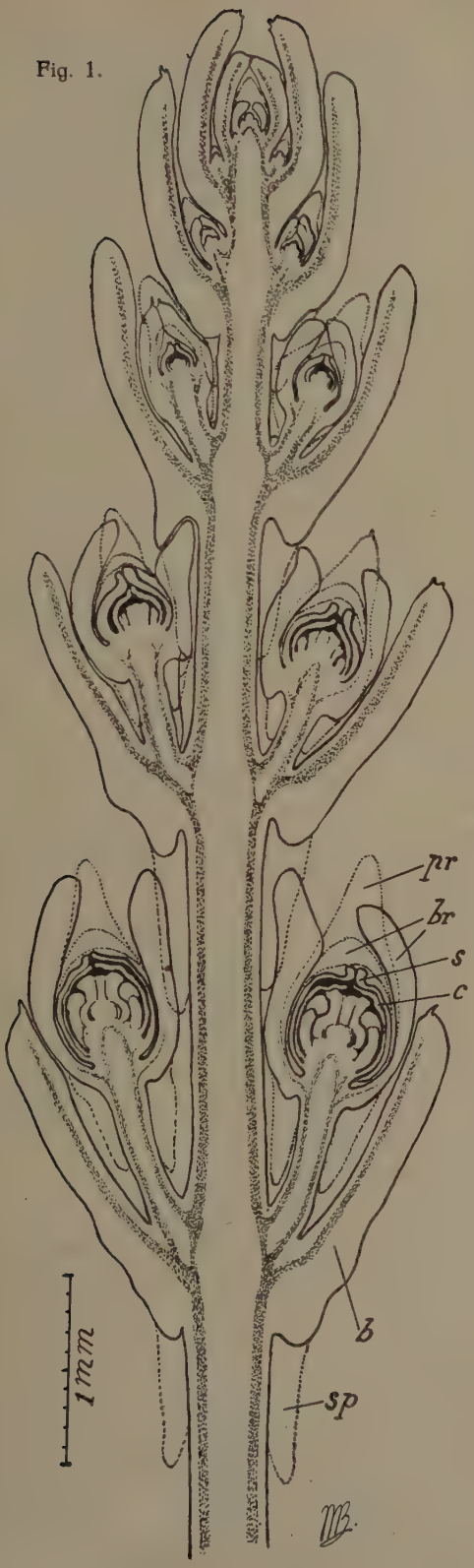
Er blijkt dus bij den lengtegroei van den jaarscheut, — welke in ons land meestal van Maart tot November, met perioden van snelleren en langzameren groei en strekking plaats heeft, — één bepaalde periode voor te komen, waarbinnen bloemknoppen worden gevormd uit het terminale groeipunt der zijscheuten. Deze periode valt in ons land in de maand Juni, d.w.z. dan eerst worden uit het meristeem de eerste herkenbare primordiën van de kelkbladen afgescheiden.

Nu zijn er van *Calluna* een aantal vormen bekend met zeer ver uiteenliggende bloeitijden. De vroegstbloeiende planten uit ons land vertoonen eind Juni en de eerste dagen van Juli reeds geopende bloemen. Een dezer vroegbloeiende tuinvormen, n.l. fa. *tenuis*, bloeit in den herfst meestal een tweede maal met hier en daar verspreid staande bloemen aan het einde van rijkbebladerde kortloten. Daar tegenover staan buitengewoon laatbloeiende vormen, waarvan de eerste bloemen zich pas in de tweede helft van October openen en die doorbloeien totdat ten slotte een strenge vorstperiode er een einde aan maakt. De planten hebben dan nog vele gesloten bloemknoppen. Bij laten winterinval bloeien zij nog met Kerstmis, soms nog later. Vooral Zuid-Europeesche vormen van *Calluna*, zooals de fa. *elegantissima* (Sennen) uit Spanje, Portugal en Marokko kunnen bijzonder laat bloeien, ook in hun eigen land (Nov.—Dec.).

Als nog extremer kan een tot de vormengroep der *multibracteata* behoorende plant uit Drente worden beschouwd. Deze vertoonde vóór den winter uitsluitend bracteeënpakjes, maar geen enkele bloem. In het daarop volgende voorjaar (Mei—Juni) echter ontwikkelden zich, hier en daar, opengaande en overigens normale bloemen. Al deze van het type afwijkende vormen naar de periodiciteit der bloemvorming moeten hier verder buiten beschouwing worden gelaten.

Wij keeren dus terug tot den meer normalen toestand. Begin Juni zijn meestal de eerste perianthkransen aanwezig. Het is echter moeilijk de eerst aangelegde bloemprimordia op te sporen aan de rijkvertakte langloten,

Fig. 1.



want het basale gedeelte heeft, zooals wij reeds zagen, uitsluitend assimilatieloten. Bovendien blijven de aan de zijscheuten van de tweede en derde orde gevormde bloemknoppen achter bij de hoogerop geplaatste bloemknoppen aan zijscheuten van de eerste orde. Men ziet dit duidelijk gedemonstreerd bij krachtig ontwikkelde planten, in het begin van den bloeitijd. De bloemknoppen aan de vertakte zijscheuten gaan pas open als de eerste bloemen aan onvertakte zijscheuten reeds in vollen bloei zijn of zelfs al uitgebloeid zijn. Dit laatste komt voor, indien de zijscheuten lang zijn en op hun beurt weer vertakkingen vertoonen. Men krijgt den indruk, dat de tijd, die noodig is voor het aanleggen van de talrijke bladprimordia van deze langere zijscheuten de vorming van de bloemknoppen daaraan heeft vertraagd.

De bloemaanleg bij *Calluna* heeft dan ook niet simultaan, doch succedaan plaats, aan iederen jaarscheut afzonderlijk beschouwd, en wel over een tijdvak, dat zeker eenige weken kan duren, al naar gelang de lengte van den jaarscheut, het te vormen aantal bloemen en de overige omstandigheden dat meebrengen. Op Fig. 1 is de succedane bloemknopvorming gedemonstreerd. Deze mediane lentecoupe door het apicale deel van een jaarscheut op 25 Juni vertoont reeds een vrij volledige reeks van bloemknopstadia,

vanaf groeipunten, waaraan nog geen bloemdeel-primordia te onderkennen zijn tot reeds gesloten bloemknoppen toe.

De kleinheid der eerste bloemknopstadia en de waarschijnlijk hiermede in verband staande zeer snelle opeenvolging dier stadia, zouden een obstakel vormen bij de opsporing er van, ware het niet, dat juist gedurende de periode van aanleg regelmatige, dicht opeengepakte reeksen van stadia zich bevinden aan het topgedeelte der jaarscheuten. Hierdoor wordt het mogelijk door microtoomcoupes ineens knopseriën in opeenvolgende stadia bloot te leggen en door extrapolatie vast te stellen, waar nog een ongedifferentieerd bloemknopprimordium aanwezig is, n.l. daar, waar het laatste bracteeënpaar juist wordt afgescheiden (Fig. 5) en waar de eerste perianthkrans in aanleg zichtbaar is (Fig. 6).

Achtereenvolgens zullen hier nu 10 stadia worden besproken, welke gemakshalve zijn onderscheiden, maar geenszins stilstandsperioden beduiden. Stilstandsperioden komen misschien wel voor, maar zijn dan afhankelijk van uitwendige invloeden, zooals koude, droogte, verwondingen enz. Onder stadium zal hier worden verstaan een ontwikkelingstoestand, die gekenmerkt wordt door bepaalde, voor het eerst zichtbaar geworden, primordia, organen of orgaandeelen. Tusschen de stadia liggen dan de ontwikkelingsperioden.

Stadium I. (zie Fig. 5). Hierbij is het laatste paar bractee-primordia afgescheiden, d.w.z. zichtbaar geworden. Het ± half bolvormige vegetatiepunt is nog glad en heeft een diameter van 60—70 μ gekregen, is dus iets grooter dan de gewone vegetatieve groeipunten, die 40—60 μ diameter hebben op het moment, dat juist weer een paar bladprimordia is afgescheiden, zooals in Fig. 4 (zie figurenverklaring).

Stadium II. (Fig. 6). De vier kelkblad-primordia zijn zichtbaar. Evenals op Fig. 5 wordt het bloemprimordium voorafgegaan door 3 bracteeënparen en één paar prophyllen. Dit geheel vult den bladhoek van een gewoon langlotblad en is verder gelegen tusschen het langlotinternodium, het steunblad en de beide sporen van het daarboven geplaatste steunblad. Het nog ongedifferentieerde of beter: nagenoeg ongedifferentieerde, groeipunt binnen de 4 kelkbladprimordia heeft nu een diameter van ca. 100 μ gekregen en begint zich zwak kegelvormig te welven.

Stadium III. (Fig. 7, 8 en 10). De 4 kroonslip-primordia zijn zichtbaar geworden in de hoeken tusschen de kelkblad-primordia, alterneeren dus daarmede. Ook de kroonwal is even zichtbaar, terwijl van meeldraadprimordia nog niet veel te zien is, al zijn zij aanwezig, zooals blijkt uit Fig. 7. Hier krijgt men den indruk, dat de meeldraad-primordia reeds eerder dan of gelijktijdig met de kroonslip-primordia worden aangelegd, wat ook bij andere *Ericaceae* is geconstateerd; men vergelijke hiertoe o.a.: LUYTEN en VERSLUYS (1921), p. 108 en Fig. 15. Het groeipunt heeft zich nu iets gerekt en heeft een diameter van ca. 120 μ, terwijl de geheele bloemknop ca. 200 μ diameter heeft.

Stadium IV. (Fig. 11). Ik heb geen stadium kunnen vinden, waarbij

slechts één krans van 4 meeldraden zichtbaar was, zonder meer. Toch zal op een gegeven moment deze toestand moeten voorkomen, naar alle waarschijnlijkheid. Vermoedelijk heeft hier de vorming der uiterst kleine primordia zeer snel achtereen plaats, zoodat dit tusschenstadium aan de waarneming is ontsnapt en de indruk wordt gewekt van een nagenoeg simultaan optreden der 8 meeldraad-primordia. Evenmin kon worden uitgemaakt welke krans het laagst lag, de epipetale of de episepale. Bij *Rhododendron* schijnen de episepale, dus de met de kroonslippen alterneerende, het eerst aanwezig te zijn. De meeldraad-primordia hebben nu een diameter van 30—50 μ, terwijl de cellen van het meristeem, in de deelingszône 4—5 μ lang zijn. De kern vult dan nagenoeg de geheele cel op. Het aantal cellen in een meeldraad-primordium zal $\pm$ 50 bedragen.

Als stadium IV heb ik dan ook aangenomen den knoptoestand, waarbij de krans van 8 meeldraad-primordia goed zichtbaar is. Nu is het opvallend, dat de 4 episepale knobbels meer bolvormig zijn afgerond, terwijl de epipetale meer ovaal in doorsnede zijn. Hieruit vallen echter geen verdere conclusies te trekken, want vormverschil kan voortspruiten uit de drukverhoudingen welke op dat moment heerschen rondom het primordium, maar ook uit een hoogere of lagere ligging. Aan de microtoomcoupes, die uitsluitend voor dit onderzoek werden gebezigd was dit niet uit te maken. Van een differentiatie van het gynaecium is nog geen sprake. De bloemknop heeft nu een diameter van 250—300 μ gekregen. Hier moet er tevens op worden gewezen, dat de lengtecoupes van Fig. 7 en 8 betrekking hebben op bloemknoppen, voorafgegaan door slechts 2 bracteeënparen, terwijl op de dwarscoupen van Fig. 10 en 11 drie bracteeënparen voorkomen. Het aantal bracteeën wisselt bij *Calluna* vrij sterk, ook wel aan één en hetzelfde individu.

Stadium V. (Fig. 9). Het gynaecium-primordium is nu als zoodanig te herkennen aan de apicale afplatting en verbreeding. Evenals op Fig. 7 en 8 reeds zichtbaar is, heeft het bovenste bracteeënpaar zich over den bloemknop gewelfd, maar nu hebben ook de kelkbladen elkaar bereikt en dekken de overige bloemdeelen toe, — aanvankelijk door over elkaar te schuiven met hun toppen, zooals op Fig. 9 en 12 zichtbaar is. De diameter van den bloemknop is thans ca. 350 μ.

Stadium VI. (Fig. 12 en 16). Aan den top der meeldraad-primordia hebben de antheren-knobbels zich nog niet gevormd, maar de kroonslippen beginnen zich over de stempelvlakte te buigen, terwijl in het vruchtbeginsel-primordium een flauwe afteekening der vier hokken van de doosvrucht is te zien, waarmede tevens de obdiplostemonie, zooals die bij de *Ericaceae* voorkomt, is aangeduid. Het gynaecium heeft zich met den meeldraad- en kroonkrans tegelijk gestrekt, zonder dat nog een feitelijke differentiatie tusschen vruchtbeginsel en stijl is te zien. Wel begint de stempelvlakte zich wat meer te plooien. De bloemknop heeft nu ca. 380—400 μ diameter. Op Fig. 16 wordt de bloemknop voorafgegaan door een grooter aantal gewone loofbladen, zooals dit vaak voorkomt.

Stadium VII. (Fig. 13). Nu zijn de helmknop-primordia goed te herkennen, maar de aanhangsels daarvan zijn nog niet zichtbaar. Ook de placenta is nog niet goed zichtbaar, echter wel de plooien van het stijlkanaal en de eerste aanleg der nectariën. De kroonslippen hebben elkaar nu ook bijna bereikt boven het stempelvlak. Aan den top der kelkbladen hebben zich kussenvormige verdikkingen gevormd (zie ook Fig. 14 en 15). De in de breedte uitgroeiende kelkbladen gaan zich nu paarsgewijs om elkaar heen leggen, daar zij meer dan den halven omtrek beslaan. De bloemknopdiameter is nu ± 0,5 mm.

Stadium VIII. (Fig. 14). Ook de aanhangsels der helmknoppen worden nu zichtbaar, terwijl de placenta en de nectariënkussens eveneens duidelijk waarneembaar zijn. De geheele bloemknop begint zich te strekken, de stijl blijft de meeldraden in lengte voor. De bracteeën wijken steeds meer uiteen. De bloemknopdiameter is thans ca. 0,7 mm.

Stadium IX. (Fig. 15). De geheele bloemknop heeft zich zoowel gestrekt als verbreed. De kelkbladen zijn langer dan de bracteeën geworden. De sepalen beginnen zich wit te tinten en zijn direct aan de plant waarneembaar door het uiteenwijken der bracteeën. In dit stadium vinden de reductiedeelingen der pollentetraden plaats en is de embryosack-moedercel aanwezig. Bloemknopdiameter ca. 1 mm.

Stadium X. (Fig. 18). De bloemknop heeft haar vollen wasdom als zoodanig bereikt en heeft 3—5 mm lengte. De sepalen hebben zich roseviolet getint. De helmdraden hebben hun karakteristieken S-vorm aangenomen. De aanhangsels der helmknoppen zijn gekamd, terwijl de helmknoppen zich meestal reeds geopend hebben met een zijdelingsche spleet, waardoor de pollentetraden naar buiten treden. Alles is nu gereed voor de anthese, die normaal op onze breedte plaats vindt van midden Juli tot eind Augustus of begin September.

Zooals reeds eerder opgemerkt bestaan er bij *Calluna* groote fluctuaties in den bloeitijd (van eind Juni tot nieuwjaar en zelfs tot het volgende voorjaar). Deze verschillende bloeitijden treden bij de *Ericales* meer op.

Fig. 25.

Erica carnea bijvoorbeeld vormt eveneens in Juni haar eerste bloemknoppen (zie: CHURCH, (1908), p. 138, Fig. 2), en overwintert in normale gevallen met volledige bloemknoppen van het hier besproken stadium X.

Toch zijn er verschillende vormen van deze soort die hetzij vóór den winter reeds tot bloei komen of later in het voorjaar pas bloeien. *Erica tetralix* bloeit dikwijls twee maal in hetzelfde groeiseizoen, terwijl de bloeitijd van *Erica cinerea* zeer lang gerekt kan zijn en

van Juni tot in den winter kan duren bij de verschillende vormen. *Calluna* echter vertoont wel de grootste spelingen, of het zou moeten wezen dat deze soort thans het best onderzocht is.

Ook morphologisch vertoont *Calluna* in haar bloemen een groot aantal afwijkingen van het gewone type, zoowel wat variatie in de knopligging betreft, — waarvan enkele voorbeelden in Fig. 16, 20 en 25 zijn weergegeven, — als in het aantal der bloemtwijgbladen, bracteeën, sepalen, kroonslippen, meeldraden en stijlen. Niet alleen treden deze afwijkingen dikwijls locaal aan één individu op, maar zijn voor het meerendeel ook als erfelijk gefixeerde vormen met bepaalde afwijkingen in den bloembouw bekend geworden. Hier heb ik mij echter beperkt tot de meer algemeen voorkomende gevallen.

Wijster (Drente), 21 Februari 1937.

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DIE PERIODIZITÄT DER BLÜTENBILDUNG BEI CALLUNA VULGARIS (L.) HULL.

(Zusammenfassung.)

Die ersten Blütenprimordien von *Calluna* werden auf unserer Breite normal in Juni gebildet. Sie stehen vereinzelt, terminal an beblätterten Kurztrieben, welche meistens Seitenaxen erster, zweiter und selten dritter Ordnung eines Langtriebes (Jahrestriebes) darstellen.

An einem kräftig entwickeltem Jahrestrieb kann man während der Blütezeit drei Abteilungen unterscheiden:

erstens, ein baseler Teil mit nur beblätterten Seitenzweigen 1er, 2er oder selten 3er Ordnung;

zweitens, ein zentraler Teil mit Blüten führenden, beblätterten Seitenzweigen 1er, 2er und 3er Ordnung;

drittens, ein apikaler Teil ebenfalls nur mit Assimilationstrieben.

Es gibt also eine bestimmte Periode wo Blütenknospen gebildet werden.

Die Blütenknospen an den Abzweigungen eines Jahrestriebes werden sukzedan während längerer Zeit (bis mehreren Wochen) gebildet. Mitte Juni kann man mit Hilfe medianer Mikrotomschnitten durch das apikale Ende des Jahrestriebes ganze Serien von Blütenknospenstadien zu sehen bekommen, welche es ermöglichen, die Entwicklung zu verfolgen. Fig. 1 stellt ein solcher Schnitt am 25sten Juni da.

Es werden 10 verschiedene Stadien bei der Blütenbildung unterschieden und näher karakterisiert (Sehe weiter die Figuren und die Figurenerklärung).

Es gibt bei *Calluna* viele Abweichungen vom normalen Fall. Die am frühesten blühende Pflanzen fangen bei uns schon Ende Juni, Anfang Juli mit der Anthese an. Eine frühe Gartenform (fa. *tenuis*) blüht im Herbste meistens zum zweiten Male mit nur wenigen Blüten. Die südeuropäische Formen der *elegantissima*-Gruppe fangen meistens erst in Oktober oder November zu blühen an. Eine Pflanze der *multibracteata*-Gruppe zeigte vor dem Winter nur Brakteenpäckchen, während im Frühjahr (Mai-Juni) sonst normale Blüten sich an dieser Pflanze entwickelten. Auch in der Knospenlage und in der Zahl der Blütenzweig-Blätter, Brakteen, Kelchblätter, Kronzipfel, Staubgefässe und Griffel gibt es viele Abweichungen, nicht nur lokal an einem Individuum, sondern auch als erblich fixierte Formen mit ausschliesslich einem bestimmtem Typus dieser abweichenden Blüten.

FIGURENERKLÄRUNG.

b = Stützblatt (Tragblatt)
sp = Sporn des Stützblattes
pr = Prophyllum
br = Braktee
s = Kelchblatt
c = Kronzipfel
st = Staubgefäss
g = Gynoeceum
o = Jahrestrieb (Hauptaxe)
× = Stützblatt am Jahrestriebe
× = Prophyllum

Die Figuren beziehen sich alle auf *Calluna*.

Fig. 1. Medianschnitt durch das apikale Ende eines Langtriebes am 25sten Juni.
Fig. 2. Medianschnitt durch einen lateralen Vegetationspunkt im Winter (5 Jan.).
Fig. 3. Medianschnitt durch die Spitze eines Langtriebes befor Blum-Primordien zu erkennen sind (Anfang Juni).
Fig. 4. Querschnitt gerade über dem terminalen Hauptvegetationspunkt eines Kurztriebes im Winter (Januar), die Knospenlage der Blätter zeichend.
Fig. 5. Querschnitt gerade über einer Blütenanlage, sofort nach der Bildung der Anlagen des letzten Brakteenpaares (Stadium I).
Fig. 6. Querschnitt gerade über einer Blütenanlage nach Abgrenzung der 4 Kelchblattprimordien (Stadium II).
Fig. 7. Medianschnitt durch eine Blütenanlage nach Bildung der Kelchblatt- und Kronzipfelprimordien. Es sind hier auch die Staubgefässprimordien schon gut zu erkennen (Stadium III).
Fig. 8. Wie Fig. 7, aber etwas später, — die Kronzipfelprimordien sind schon etwas grösser.
Fig. 9. Medianschnitt durch eine Blütenknospe nach Ausbildung des Stempelprimordiums. Die Spitzen der Kelchblätter haben einander erreicht (Stadium V).
Fig. 10. Querschnitt gerade über einer Blütenanlage mit ausgebildeten Kronzipfelprimordien. Die Staubgefässprimordien waren hier kaum sichtbar (Stadium III).
Fig. 11. Querschnitt durch eine Blütenanlage mit 8 im Kreise gestellten Staubgefässprimordien (Stadium IV).
Fig. 12. Medianschnitt durch eine schon geschlossene Blütenknospe in dem Moment, wo die Kronenzipfel anfangen sich über die Stempelfläche zu wölben. Die Staubgefässe sind zurück geblieben (Stadium VI).
Fig. 13. Medianschnitt durch eine Blütenknospe nach Anlage der Antherenprimordien und des Griffelkanals (Stadium VII).
Fig. 14. Medianschnitt durch eine Blütenknospe beim Anfang der Plazentabildung und mit Anfängen der Antheren-Sporen (Stadium VIII).
Fig. 15. Medianschnitt durch eine Blütenknospe von 1 mm Durchmesser. Die Kelchblätter fangen an sich zu färben und sind zu Tage getreten weil die Brakteen aus einander weichen und die Knospe sich beträchtlich verlängert hat (Stadium IX).

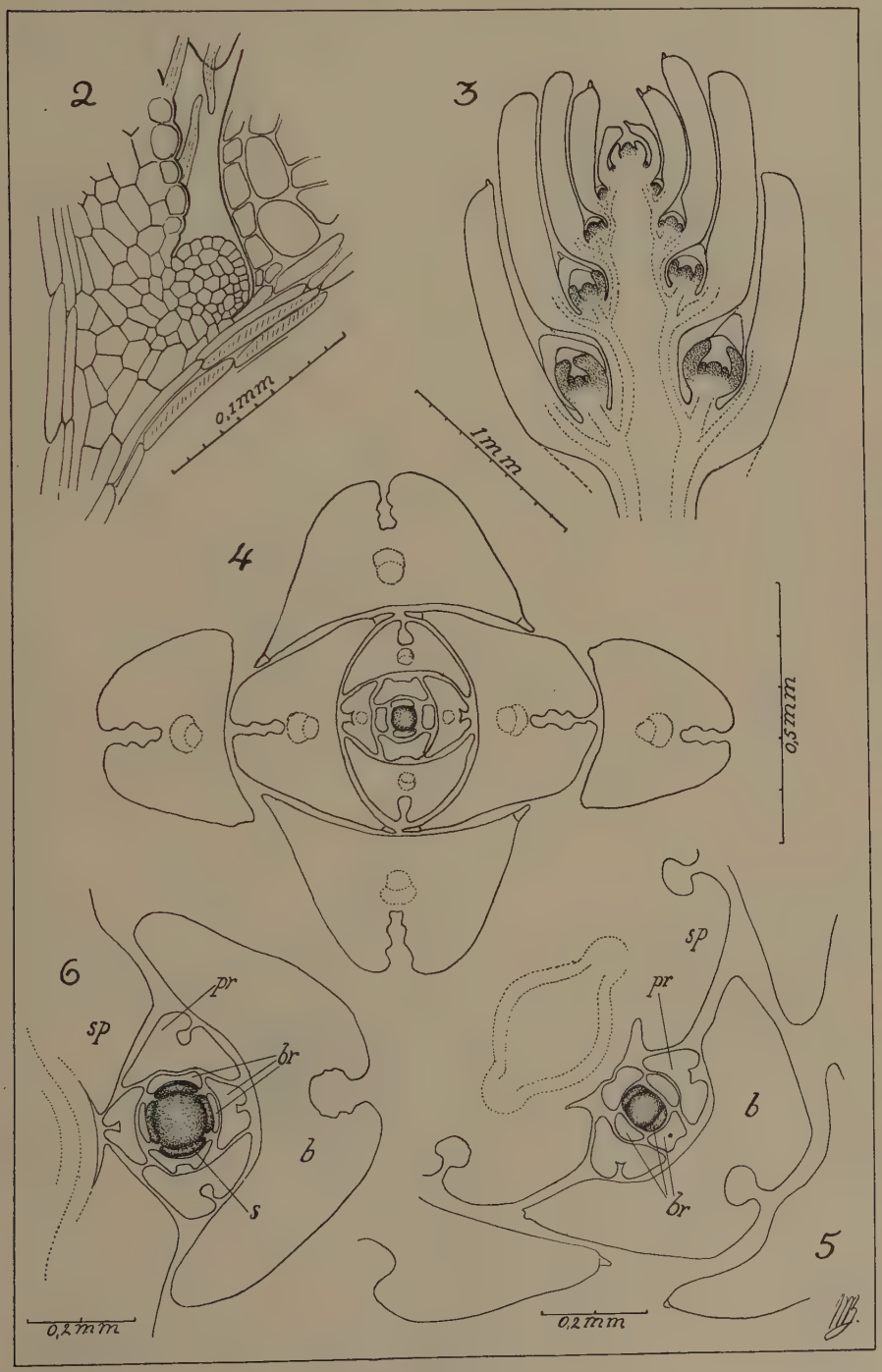

Fig. 2—6.

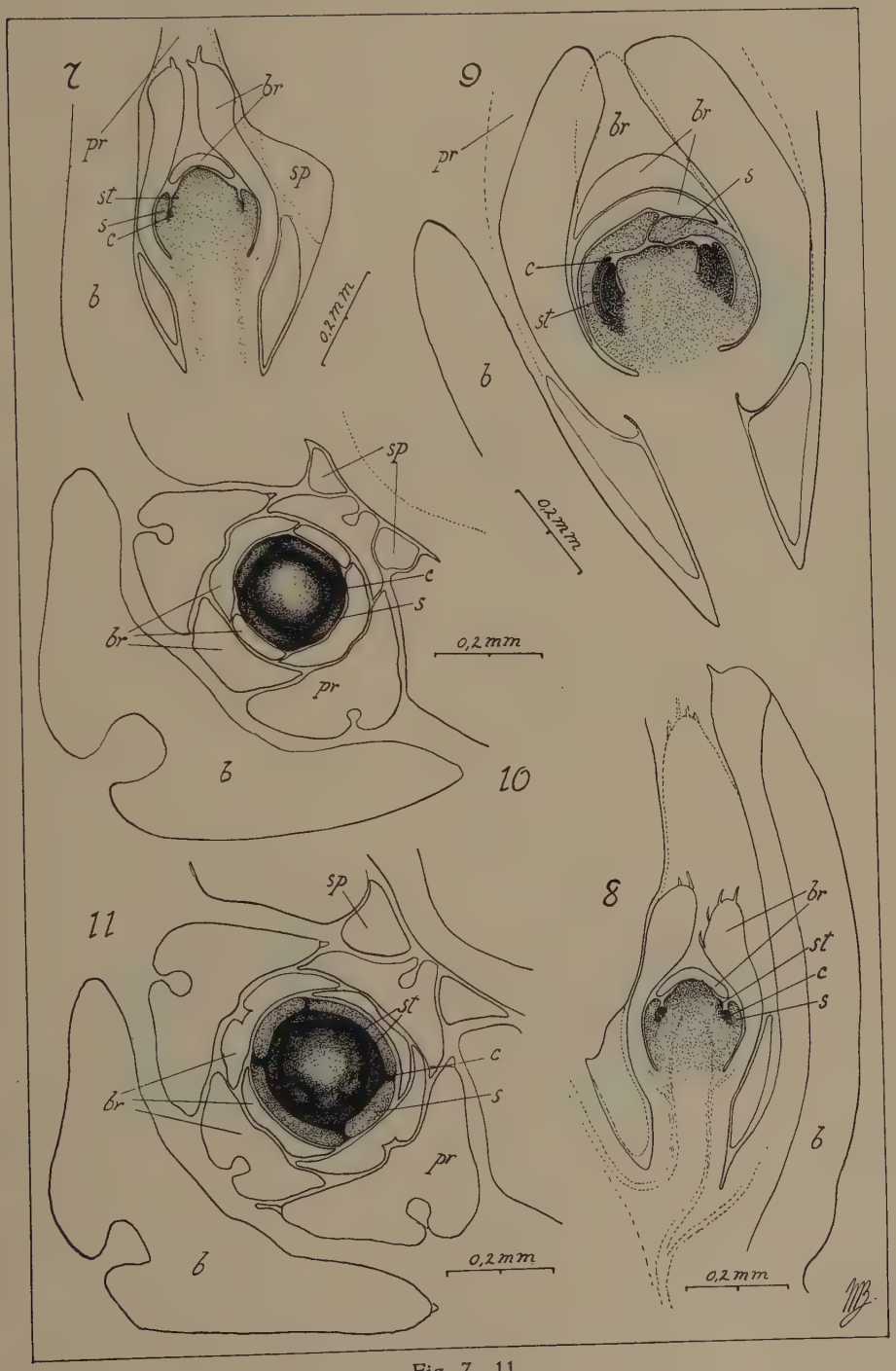
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Fig. 7—11.

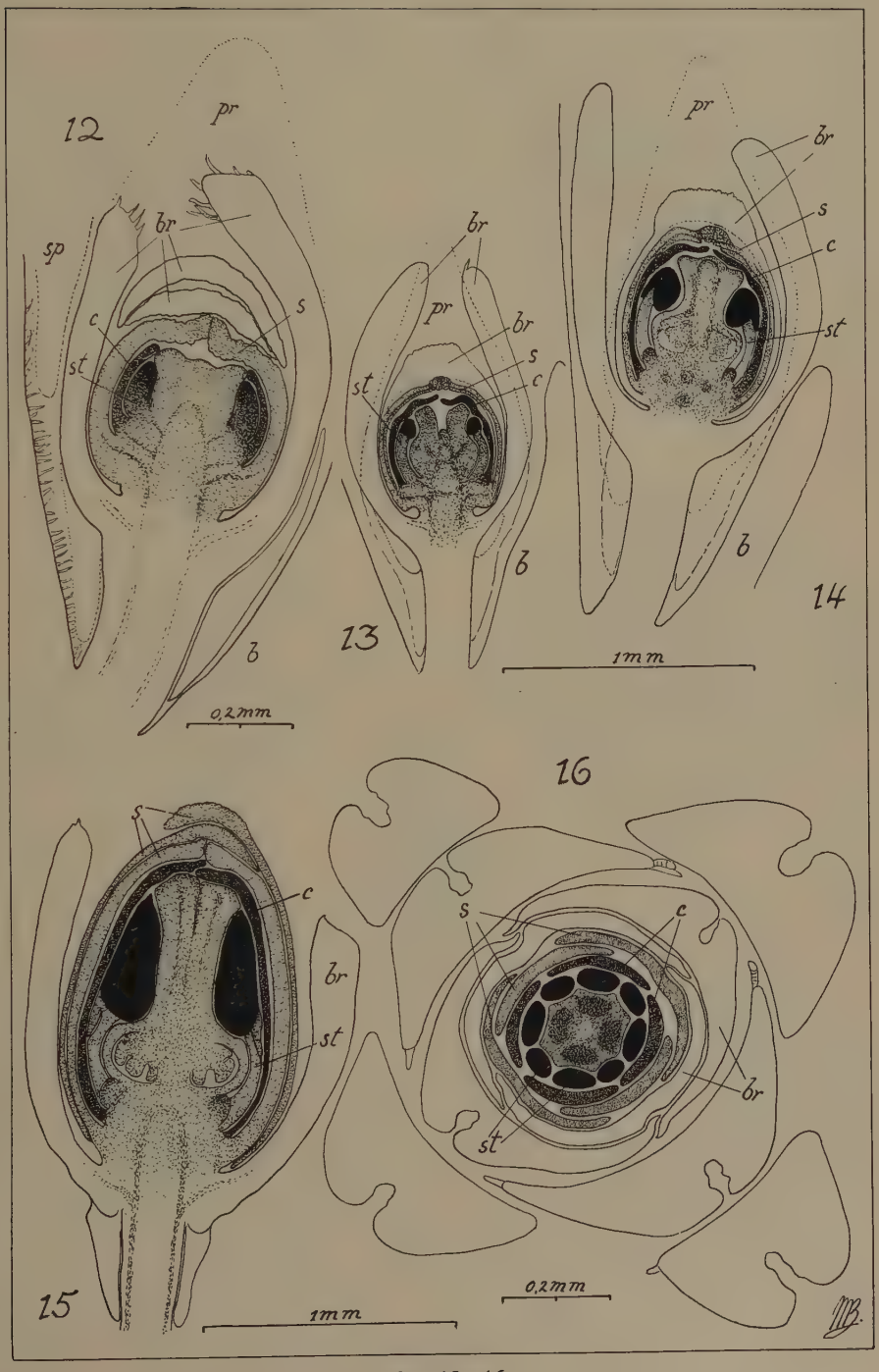
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Fig. 12—16.

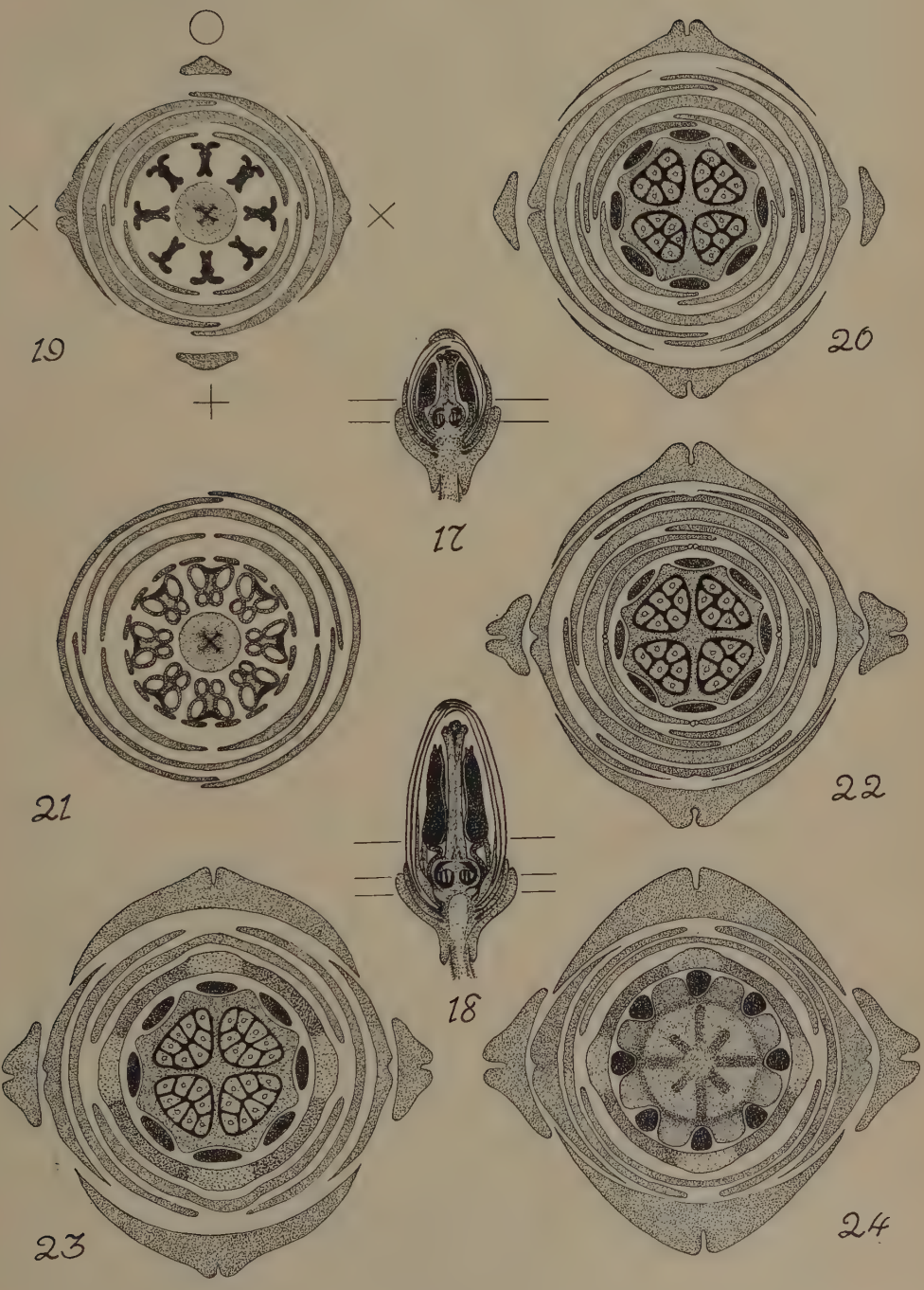

Fig. 17—24.

Fig. 16. Querschnitt durch eine Blütenknospe im Stadium VI. Die Knospe steht hier am Ende eines mehrblätterigen Kurztriebes. Die Obdiplostemonie tritt hervor in der vierfächerigen Fruchtanlage.

Fig. 17 und 18. Längschnitte durch Blütenknospen in bezw. den Stadien IX und X (vollendet) mit Angaben der Querschnitthöhen der Figuren 19—24. Beim Stadium X sind die Filamenten S-förmig gekrümmt und die Antherensporen völlig ausgebildet. Die Streckung ist beendet, die Antheren haben sich oft schon geöffnet vor der Anthese.

Fig. 19—24. Etwas schematisierte Querschnitte durch Blütenknospen, die Lage der Teile zeichend. Die Figuren 20 und 22 beziehen sich auf zwei verschieden aufgebauten Knospen, — die Schnittebene ist fast die gleiche. — In Fig. 22 ist gerade die Höhe getroffen, wo die Kronzipfel noch verwachsen sind, während hier drei Brakteenpaare anstatt deren zwei zugegen sind. Das Übrige ergiebt sich aus den Figuren.

Fig. 25. Querschnitt durch eine Blütenknospe im Stadium X, zur Höhe der Plazenta.

Botany. — *Notes on some physical properties of Chlorophyll films.* By E. A. HANSON. From the Botanical Institute, University of Leyden. (Communicated by Prof. L. G. M. BAAS BECKING).

(Communicated at the meeting of February 27, 1937).

Chlorophyll ($a + b$) was prepared from nettle leaves according to WILLSTÄTTER and STOLL. By working as quickly as possible — expecially by allowing only the shortest possible time for adsorption — allomerisation was finally prevented. The chlorophyll, dissolved in petroleum ether — acetone mixture (2 : 15), was spread in a monomolecular film in a LANGMUIR apparatus in the usual way on aqueous solutions, ranging in p_H from $p_H = 3 - 11$. Diluted HCl, the veronal-buffer-mixture of MICHAELIS and the glycine-buffer-mixture of SÖRENSEN were used.

The chlorophyll molecule (fig. 1) consists of two parts: the "colourless" phytol-chain and the "coloured" nucleus. The former part has no affinity to water, whereas the nucleus possesses several hydrophilic groups, of which the "active carbon five ring" may be considered as the most important, the magnesium-centre being less active. The two COOH groups are esterified with phytol and methanol respectively and therefore need not to be considered here.

If the four pyrrol-groups are assumed to be situated in one plane, an estimation of the "spreading area" of a single "coloured nucleus" may be made, using HENGSTENBERG and MARK's data for inter atomic distance of various types of bonds. This surface area proves to be $100 - 110$ Å^2. Preliminary work of Professor E. GORTER, quoted by HUBERT 1935 yielded similar values.

The smallest surface, measured by spreading, proved to be 106 Å^2 at $p_H = 4.4$, indicating the possibility that the "coloured nucleus" might be actually a *plane* structure. *X*-ray analysis of our preparations carried out

at the Laboratory for Inorganic Chemistry, Leiden, showed the amorphous nature of Chlorophyll $(a + b)$. However, one very strong reflection,

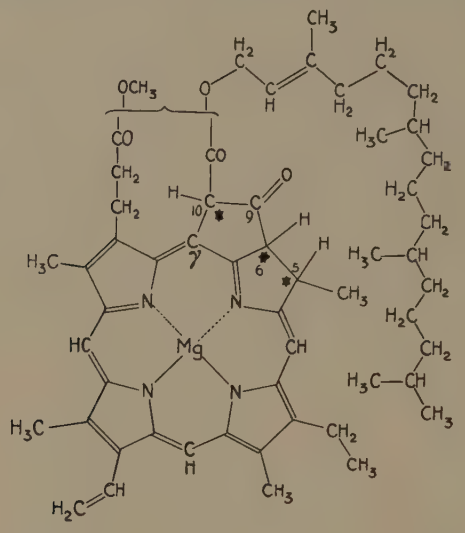

Fig. 1. Chlorophyll *a*, after ARTHUR STOLL 1936.

belonging to a period of 4.2 Å was observed, the second order of which was also faintly visible.

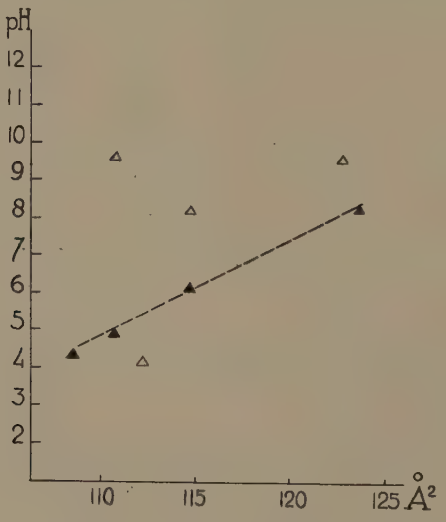

Fig. 2. Relation between molecular surface and p_H. At $p_H = 8.2$ and 9.8 two surfaces correspond to the linear parts before and after the discontinuity. In the pressure-area curves given in figure 3. At $p_H = 4.0$ the increase in surface is due to the formation of phaeophytin.

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[1]) I want to express my gratitude for the help and advice given to me by Dr. J. A. A. KETELAAR, Privat-Docent at that Institute.

This reflection can only be explained if the four pyrrol rings are situated in one plane. For the short peripheral methyl-ethyl and vinyl side chains(see fig. 1) will increase the thickness of the flat disc to about 4.2 Å. *X*-ray analysis of an amorphous compound cannot yield the data necessary to determine whether all the atoms of the "disc" are situated in one plane. For our purpose, however, the precision is quite satisfactory.

The correspondence between the calculated surface-area on the one hand and both the spreading-area and the results from te *X*-ray analysis on the other, warrant the conclusion that the coloured part of the chlorophyll-molecule, whether spread out in a film or in the solid state — is flat and, in the case of the film, placed horizontally in the water — air interface. The presence of hydrophilic groups in the nucleus, however, might cause the adsorption of so much water that even a "tilted" nucleus might show a large spreading-surface. While the dicarbonic acid-chlorophyllid is soluble in water, the monomethylcarbonic acid-chlorophyllid is soluble in 0.01 n. KOH, the dimethylchlorophyllid is insoluble in water and the hydratation of the nucleus may, therefore, not be able to exert much influence.

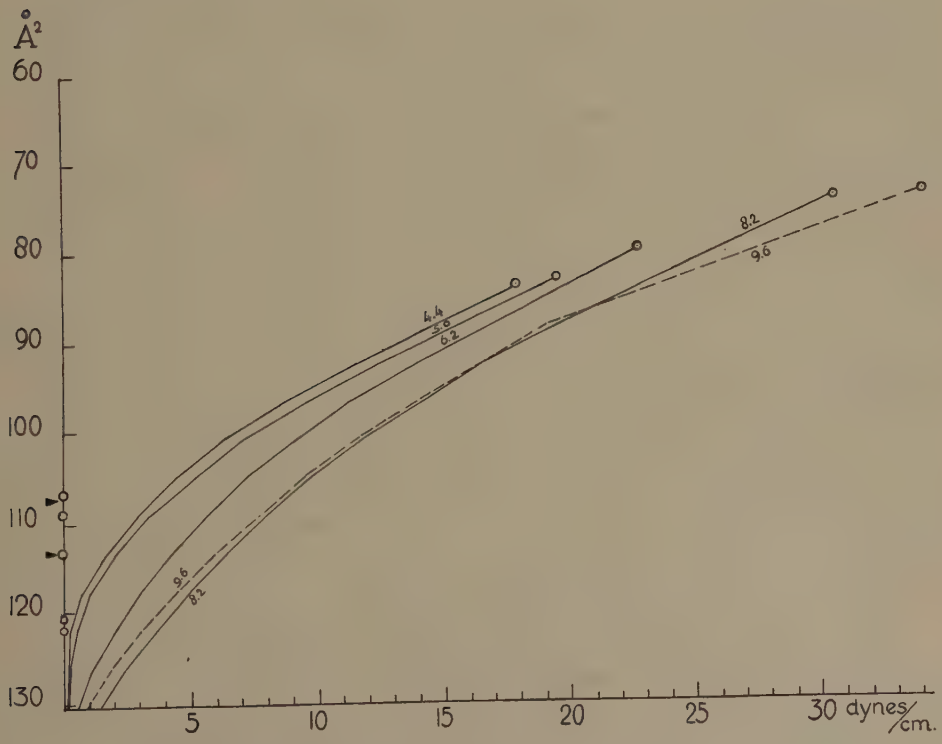

Fig. 3. Pressure-area curves for chlorophyll $(a + b)$. The interrupted curve at $p_H = 9.6$ shows the first marked discontinuity at a pressure of 19 dynes/cm. The curve of $p_H = 8.2$ shows an indication of a discontinuity. The circles on the ordinate indicate the extrapolated surface area of the chlorophyll after the discontinuities at $p_H = 8.2$ and 9.6 occur.

The molecular surface area, as measured by spreading increases gradually with increasing p_H from 4.4 — 8.5 from 106 — 123 Å² as a result of hydratation (see fig. 2). This result is in agreement with STOLL's idea that the chlorophyll molecule is fixed in the chloroplastin to a basic synergon. At least we may conclude that a high p_H will favour the supply of assimilationwater in the living plant (see also VAN NIEL).

The curves showing the relation between molecular surface and pressure (fig. 3) show, for the spreading at $p_H = 9$, a sudden break at ± 18 dynes/cm. Increasing p_H's bring two and even three breaks. This may be interpreted by the assumption that at these high alcalinities the dehydration of the hydrated chlorophyll molecules by pressure occurs discontinously, in separate steps.

Even after the last break the extrapolated molecular area is never less than the surface area found (by extrapolation) at $p_H = 4.4$. This shows that the *least hydrated form* of the chlorophyll molecule has a surface area of 106 Å². Comparison with the calculated area indicates, therefore, that at $p_H = 4.4$ chlorophyll is practically free of water.

Below this p_H the central magnesium atom is replaced by hydrogen and phaeophytin is formed. This phaeophytin evidently shows a larger surface and a higher tolerated pressure than the chlorophyll at $p_H = 4.4$ (see fig. 4).

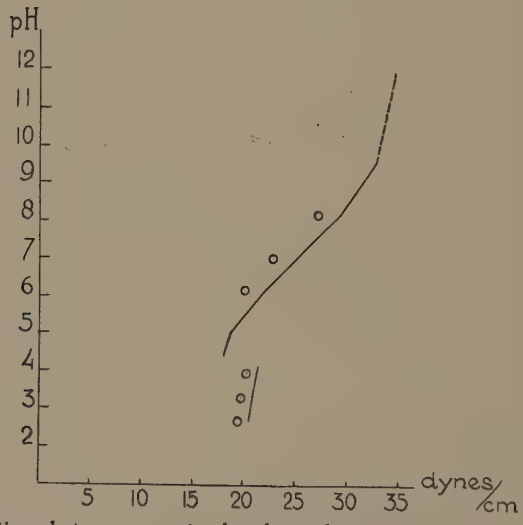

Fig. 4. Relation between maximal tolerated pressure and p_H. At $p_H = 4$ a discontinuity occurs due to the formation of phaeophytin. Drawn line: fresh preparation, circles: preparation a few days old.

The magnesium seems to counteract, therefore, the hydratation of the "carbon-five-ring". Experiments on the behaviour of phaeophytin and on the measurement of E.M.F. of monomolecular films of chlorophyll are in progress.

Leyden, February 1937.

LITERATURE.

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J. HENGSTENBERG u. H. MARK, Die Bedeutung der Röntgen Strukturanalyse im Bereich der organischen Chemie. Die Naturw. **20**, 539 (1932).

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B. HUBERT, The physical State of Chlorophyll in the living Plastid. Rec. des Trav. botan. néerl. **32**, 229 (1935).

Geology. — *Tertiary rocks from the Misool-Archipelago (Dutch East Indies).* By H. BAGGELAAR. (Communicated by Prof. L. RUTTEN).

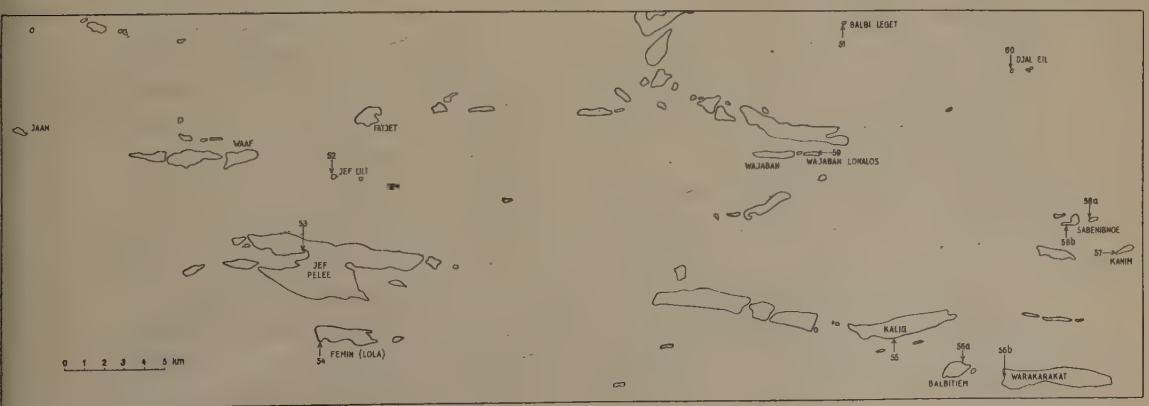
(Communicated at the meeting of February 27, 1937).

INTRODUCTION.

The material examined was collected by Dr. FR. WEBER on some little islands belonging to the Misool-Archipelago, situated south of Misool. My thanks are due to Dr. WEBER who kindly lent me the rock samples for investigation and I am indebted to the "MOLENGRAAFF-FONDS" for financial support to this publication.

On the map below the localities have been indicated with an arrow-head. The numbers on this map correspond with the numbers of the specimens in the Museum of Natural History at Basel. The thin-sections are in the geological collections of the Mining Institute at Delft.

For the greater part various samples from one place are available, but they were not taken from a continuous profile, as Dr. WEBER told me. So, if the age of one or more specimens bearing the same number has been determined, this age is (even if the other samples give no data concerning the age) a criterion for the relative age of the place to which all these specimens belong.



DESCRIPTION OF THE ROCKS.

Balbi leget (Nr. 51).

Nr. *51a* is a compact, gray limestone, for the greater part built up by numerous specimens of the genera: *Orbulina, Globigerina, Textularia, Biloculina, Quinqueloculina, Operculina, Rotalia,* and *Pulvinulina.* One vertical section of a small megalospheric *Lepidocyclina* was found. The rock contains very little quartz in small angular grains, a little glauconite and some rests of *Echinoidea* (in the shape of discs).

Nr. *51b* is a compact, gray limestone with a rounded conglomeratic inclusion of another sedimentary rock, containing some *Globigerinae, Pulvinulinae,* and quartz. It also differs from Nr. *51a* by the presence of many *Miliolidae* (among which very big specimens), many *Textulariae,* and few *Globigerinae, Pulvinulinae,* and *Rotaliae.* There are some rests of *Echinoidea* and a little quartz in angular grains.

Owing to the presence of a small megalospheric *Lepidocyclina,* the age of Nr. *51a* has been fixed on *Tertiary e* or *f.*

Jef Lili (Nr. 52).

Nr. *52.* (fig. 5). An almost white, organogenous limestone with a coarse structure, chiefly built up by *Foraminifera,* in which many *Fasciolites* could be recognized with the naked eye. The following Foraminifera were found: *Fasciolites, Flosculina, Operculina, Biloculina, Quinqueloculina, Textularia,* and *Gobigerina.* A striking characteristic is the presence of the many beautiful big *Miliolidae.* Besides, the rock contains fragments of *Lamellibranchia* and *Echinoidea.*

Owing to the presence of *Flosculina,* the age of this rock has been fixed on *Tertiary a.*

Jef Pelee (Nr. 53).

Nr. *53a* is a brownish-gray, sandy limestone, chiefly built up by rests of *Foraminifera, Bryozoa, Echinoidea, Lamellibranchia,* and *Algae.* The sandy character is caused by many angular quartz grains, while the rock also contains a little glauconite. I found some small megalospheric *Lepidocyclinae,* some vertical sections of *Heterostegina* or *Cycloclypeus,* and many *Miliolidae, Textulariae, Pulvinulinae, Rotaliae, Operculinae,* and *Globigerinae.* The rock besides contains a great many *Algae* (figs. 1 and 2) belonging to a genus (or genera) unknown to me. Besides these Algae I found some specimens of the genera *Corallina* and *Lithothamnium.*

Nr. *53b* is also a brownish-gray limestone with a moderate quantity of quartz and for the greater part built up by rests of *Foraminifera, Bryozoa, Lamellibranchia, Echinoidea,* and *Algae.* The Foraminifera belong to the genera: *Textularia, Globigerina, Pulvinulina, Biloculina, Quinqueloculina, Operculina,* and *Rotalia.* The Algae are present in very large quantities

and belong for the greater part to the forms of figs. 1 and 2. Finally some *Corallinae* and *Lithothamnia* were found.

The age of specimen *a* has been fixed on *Tertiary e* or *f*, based on the presence of small megalospheric *Lepidocyclinae*.

Femin (Lola) (Nr. 54).

Nr. *54* is a compact, gray limestone with a small amount of angular quartz grains. It is chiefly built up by the rests of small *Foraminifera, Algae,* and *Echinoidea*. By the side of large numbers *Globigerinae, Miliolidae, Textulariae,* and *Operculinae*, I found fewer specimens of *Spiroclypeus* and *Lepidocyclina*. The *Lepidocyclinae* are small, but no section was found showing the embryonal apparatus. Furthermore the rock contains rests of *Bryozoa* and the typical Algae found in the rocks from JEF PELEE. Also there is a little glauconite.

Owing to the presence of *Spiroclypeus* the age has been fixed on *Tertiary e*.

Kalig (Nr. 55).

Nr. *55a* is a very compact, fine-granular, gray, sandy limestone with rare organisms. Except for some glauconite and a moderate amount of angular quartz grains, nothing could be determined but a few *Globigerinae, Quinqueloculinae,* and some rests of *Echinoidea*.

Nr. *55b* is a brownish-gray, sandy limestone with many recent *Balanidae* and with holes bored by *Pholadidae*. It is much coarser than 55a and it appears to be almost entirely built up by *Foraminifera* (many *Globigerinae, Miliolidae, Operculinae*), rests of *Echinoidea*, and *Algae*. The *Algae*, belonging for the greater part to the forms of figs. 1 and 2, are present in large quantities. Besides, the rock contains some rests of *Bryozoa*.

Because of the absence of stratigraphically important Foraminifera, the age of the rock cannot be determined.

Balbitiem (Nr. 56a).

Nr *56a a* is a compact, gray, sandy limestone of a bedded structure. It consists of a fine-granular aggregate with some *Globigerinae* and *Biloculinae*. It contains a little glauconite.

Nr. *56a b* is a micro-crystalline limestone, in which no rests of organisms could be determined.

Nr. *56a c* is a compact, gray, bedded limestone with a small quantity of quartz, containing some *Globigerinae*, while also very little glauconite is present.

Nr. *56a d* greatly resembles specimens *a* and *c*, but it is more brittle and shows a more pronounced bedded structure. Only a few *Globigerinae* could be recognized.

About the age of the island of BALBITIEM nothing definite can be said,

since none of the rock specimens show stratigraphically important Foraminifera.

Warakarakat (Nr. 56b).

Nr. *56b a* (figs. 3 and 4) is a sandy limestone, which for the greater part is built up by *Foraminifera* and rests of *Bryozoa, Echinoidea,* and *Algae.* The amount of quartz is considerable. The Foraminifera belong to the genera *Spiroclypeus* and *Lepidocyclina,* next to which *Miliolidae, Textulariae, Operculinae,* and *Globigerinae* occur. The *Lepidocyclinae* are small, megalospheric forms. The Algae are the same as in figs. 1 and 2.

Nr. *56b b.* The second rock is a fine-granular, gray limestone without quartz, that bears the character of secundary crystallization; it contains some *Globigerinae* and *Textulariae.*

Nr *56b c/g.* These five samples are so much alike that I may summarize them as being gray or brownish-gray, sandy limestones with a varying amount of quartz. They all contain great numbers of small *Foraminifera (Globigerinae, Miliolidae, Textulariae, Pulvinulinae,* and in some cases *Operculinellae* and (or) *Operculinae).* Moreover, I found in the specimens *c, d, e,* and *g Spiroclypeï* and in the specimens *c, g,* and *f* also some small *Lepidocyclinae.* None of the *Lepidocyclinae* showed an embryonal apparatus, most of the sections being fragments. All specimens also contain rests of *Bryozoa, Echinoidea,* and *Algae.* Finally there are in the specimens *d* and *g* some fragments of *Lamellibranchia* and in specimen *f* a few rests of *Crustacea.* The Algae belong for the greater part to the form of figs. 1 and 2. Moreover, in specimen *c Lithothamnium* is present. All rocks contain quartz in angular grains; the amount of quartz is a maximum in specimen *f* (about 50 %).

Nr. *56b h* is a gray limestone without quartz. I found many *Foraminifera (Miliolidae* in many and sometimes wellshaped big specimens, *Textulariae, Rotaliae,* some sections of *Operculina* or *Operculinella,* and *Globigerinae*). It further contains some fragments of *Echinoidea.*

Nr. *56b i* is a light-gray, fine-granular limestone, clearly showing recrystallization phenomena, in which the only recognizable organism rests are some *Quinqueloculinae* and *Textulariae.*

Summarizing we may, owing to the presence of *Spiroclypeus,* fix the age of the W.-coast of WARAKARAKAT on *Tertiary e.*

From this spot Dr. WEBER also brought some rests of *Brachyura,* which are being examined by Prof. V. VAN STRAELEN at Brussels.

Kanim (Nr. 57).

Nr. *57* is a gray limestone with a small amount of quartz and with *Foraminifera:* many *Miliolidae, Textulariae, Globigerinae,* and *Operculinae,* and a few *Lepidocyclinae* and *Spiroclypeï.* The *Lepidocyclinae* are represented by small microspheric and megalospheric forms. Finally the

rock contains rests of *Bryozoa, Ostracoda,* and *Algae* (among which *Lithothamnium* and *Corallina).*

As this rock contains representatives of the genera *Lepidocyclina* and *Spiroclypeus* (the former in small megalospheric forms), we may fix its age on *Tertiary e.*

Sabenibnoe. E.-island (Nr. 58a).

Nr. *58a a* is a light-brown limestone without quartz, for the greater part built up by rests of organisms. It contains *Foraminifera* (*Lepidocyclina* and *Quinqueloculina*), many *Algae,* such as *Lithothamnium, Halimeda,* together with the forms of figs. 1 and 2, the former in beautiful big specimens, *Bryozoa* and *Echinoidea.* The rock shows recrystallization with beautiful rhombohedrons of secundary calcite.

Nr. *58a b* appears to differ from *58a a* by a smaller amount of organism rests and by a moderate quantity of quartz in big angular grains. The *Foraminifera* belong to the genera *Spiroclypeus, Lepidocyclina,* and *Quinqueloculina.* The *Lepidocyclina* is a small megalospheric form. Further some *Algae (Lithothamnium)* and a few rests of *Bryozoa* and *Echinoidea* were found in this rock.

Nr. *58a c* consists again for the greater part of rests of organisms, which may clearly be seen on a polished surface. This rock also shows beautiful rhombohedrons of secundary calcite due to recrystallization (fig. 8). The percentage of quartz is much smaller than that of specimen *b*; here, too, the quartz has the form of big angular grains. The *Foraminifera* are *Lepidocyclinae, Miliolidae,* and *Operculinae.* The *Lepidocyclinae* are small microspheric and megalospheric forms. The rock further contains large numbers of *Algae,* such as *Lithothamnium* and *Halimeda,* and also many rests of *Bryozoa and Echinoidea.*

Owing to the presence of *Spiroclypeus* together with small megalospheric forms of *Lepidocyclina,* we may fix the age of these rocks on *Tertiary e.*

Sabenibnoe. W.-island (Nr. 58b).

From the W.-island 9 calcareous rocks are available, all having a certain quantity of quartz varying from a very small to a rather considerable amount, so that some of the 9 specimens can be reckoned among the calcareous sandstones. These rocks carry numerous *Foraminifera, Bryozoa, Echinoidea,* and *Algae.* Of the Foraminifera the small genera are represented by *Miliolidae, Textulariae, Operculinae, Pulvinulinae, Rotaliae,* and *Globigerinae,* while also the stratigraphically important genera *Lepidocyclina* and *Spiroclypeus* were found. In some rocks both genera occur, in others one of them.

Nr. *58b a.* This rock is slightly different from the others in that it shows a beginning of recrystallization in the form of a mosaic-structure of calcite. Besides small Foraminifera it contains *Spiroclypeï* and small megalospheric *Lepidocyclinae (Nephrolepidinae).*

Nr. *58b b, c, e,* and *g* contain small Foraminifera and also representatives of the genera *Lepidocyclina* and *Spiroclypeus*. In the specimens *b* and *c* the *Lepidocyclinae* are megalospheric forms; in the specimens *e* and *g* I did not find sections showing an embryonal apparatus. Figs. 6 and 9 give an illustration of Nr. *58b b*.

Nr. *58b d*. In this specimen the only important genus is *Lepidocyclina*.

Nr. *58b f, h,* and *i*. In these rocks the important Foraminifera are exclusively representatives of the genus *Spiroclypeus*.

Noteworthy for their extra-ordinarily large dimensions are the *Operculinae* in the specimens *d* and *h* (fig. 10, from *58b h*).

The Algae in these rocks chiefly belong to the type of figs. 1 and 2, while also some *Lithothamnia* and *Corallinae* are present.

Owing to the presence of *Spiroclypeus* together with small megalospheric forms of *Lepidocyclina (Nephrolepidina)*, the age of the rocks from the W.-island SABENIBNOE may be fixed on *Tertiary e*.

Wajaban lonalos (Nr. 59).

Nr. *59* is a brittle, yellowish-brown, sandy, rather compact limestone with much quartz, regularly dispersed in small angular grains, and with a few *Globigerinae*.

Because of the absence of guide-Foraminifera, the age of the rock could not be ascertained.

Djal (Nr. 60).

Nr. *60a, b* are both compact, brown limestones, recrystallized in the form of a compact mosaic of calcite (fig. 7) in which here and there an indication of organism rests may be seen, which originally must have been present. The relative age can therefore not be determined.

SUMMARY.

In so far as the examination has yielded a positive result, it seems that only the rock from the island JEF LILI is of *eocene* age, while on all the other islands *Neogene* is represented, viz. *Tertiary e* on FEMIN, WARAKARAKAT and the E.- and W.-islands SABENIBNOE, and *Tertiary e* or *f* on BALBI LEGET and JEF PELEE.

With reference to the *eocene* limestone from JEF LILI the following should be noted. For the first time in the Misool-Archipelago an *Alveolina-limestone* was found by BOEHM on the islands WAAF and JAN, which are situated N.W. of the islands described above. The material collected by BOEHM was described by VERBEEK [1]). VERBEEK as well as WANNER [2]) fix

[1]) R. D. M. VERBEEK, Molukkenverslag. Jaarboek Mijnwezen, 1908. Wetensch. Ged.

[2]) J. WANNER, Beiträge zur Geologischen Kenntnis der Insel Misol. T.K.N.A.G. (2), deel XXVII, 1910.

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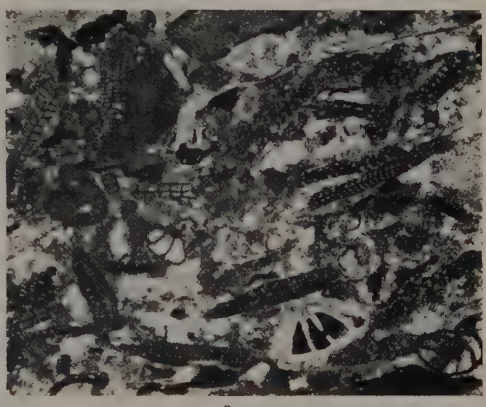

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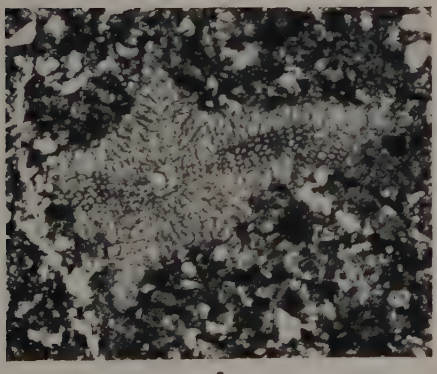

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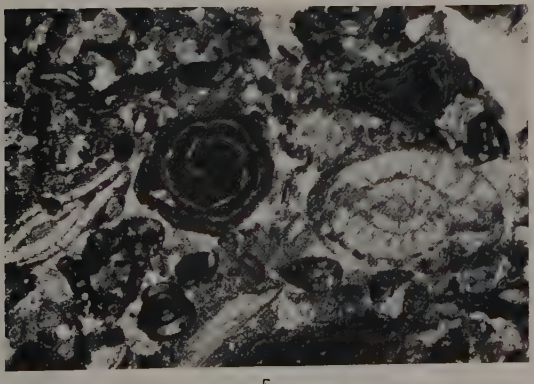

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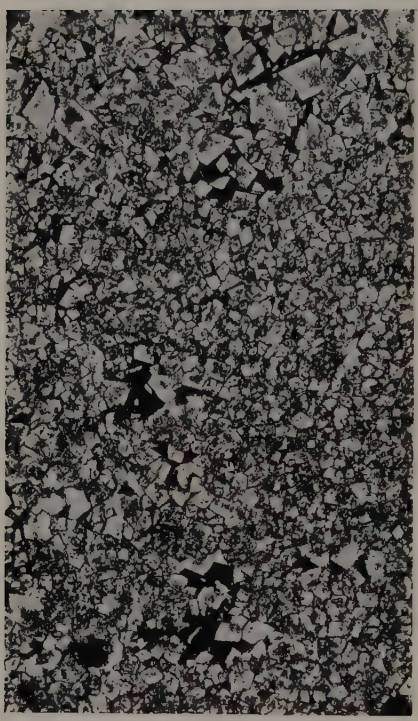

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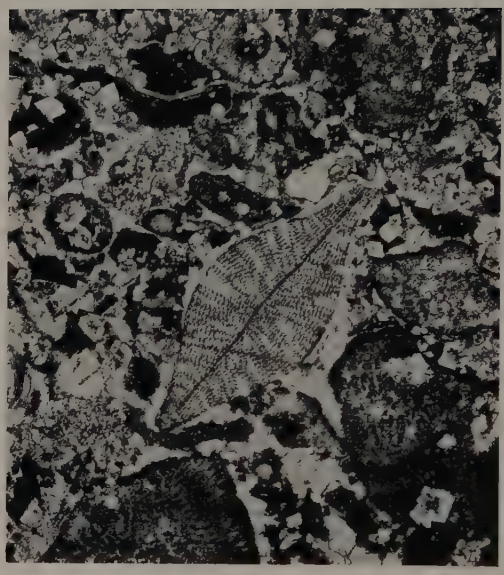

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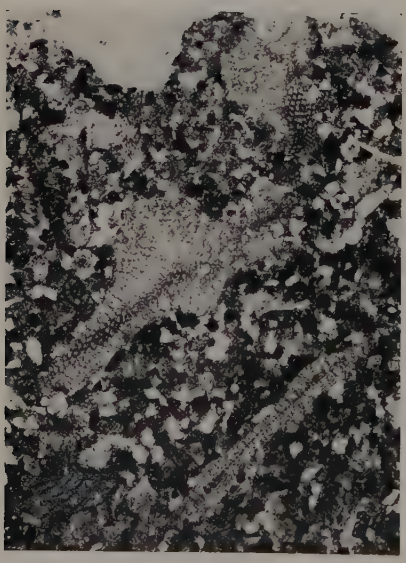

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the age of the rock on Eocene. VERBEEK writes about it: "*A microcrystalline, pure paste of calcite is entirely filled up with Foraminifera, among which Alveolinae come to the front; besides Miliolidae and some other genera, also a few sections probably belonging to Operculina. Further the Alga Lithothamnium, etc.*"

A comparison with the material of BOEHM (the original samples and thin-sections are in the geological collections of the Mining Institute at Delft) has convinced me that also the rock of JEF LILI is a typical *Alveolina-limestone.*

In the *Alveolina-limestone* collected by BOEHM on the islands JAN and WAAF as well as in those, found by WANNER on "The Saw" of MISOOL, Orbitoïdidae and Camerinae fail. Nor did I find any Orbitoïdida and Camerina in the limestone from JEF LILI. Because of the great resemblance of the *Fasciolites* examined (belonging to some different species) to those in the material of BOEHM, I think I may ascribe slight differences between these rocks and the limestone from JEF LILI to local circumstances.

Neogene deposits are mentioned by WANNER from the islands WAJABAN, SABENIBNOE, JEFNA, DARAM, and on MISOOL in the Kampong Pawô. The facies of the rocks coming from these islands may show some differences. The *neogene* rocks examined by me also show considerable differences, but all these rocks are characterized by the presence of small *Lepidocyclinae* and (or) *Spiroclypeï*. On WAJABAN WANNER found a limestone which he describes as: „*. . . Hellbräunlichen, schwarz verwitternden, knorrigen dickbankigen Kalkstein, der in manchen Handstücken an den Alveolinenkalk erinnert. U.d.M. zeigt er aber kleine Lepidocyclinen und reichlich Lithothamnien, während Alveolinen fehlen.*" (Loc. cit. 2, page 492). Such a description is entirely applicable to two examined rocks from SABENIBNOE (E.-island). About SABENIBNOE WANNER writes (Loc. cit. 2, page 492) : „*Vom Inselchen Sebenipnu erhielt ich eine Probe eines plattigen, bräunlichen, fein brecciösen Sandsteines. Dünngeschliffen erscheint er erfüllt mit Foraminiferen (Lepidocyclinen, Globigerinen, Milioliden, Rotalien, Textularien) und Lithothamnien.*" A rock that entirely answers to that description was not found in the examined collection. It is possible that some of the calcareous sandstones from the W.-island (e.g. the Nrs. *58b d, e,* or *f*) resemble it.

As remarkable facts I would finally mention the failing of *Miogypsina* in all neogene rocks examined and the sometimes considerable amount of quartz in many limestones.

EXPLANATION OF THE FIGURES.

Figs. 1 and 2. JEF PELEE. Sandy limestone with rests of *Foraminifera, Echinoidea, Lamellibranchia,* and *Algae.* 24x.

Figs. 3 and 4. WARAKARAKAT. Sandy limestone with *Spiroclypeus.* Quartz in angular grains. 24x.

Fig. 5. JEF LILI. Limestone with *Flosculina, Fasciolites, Operculina, Miliolidae,* and rests of *Lamellibranchia* and *Echinoidea.* 11x.

Fig. 6. SABENIBNOE. W.-island. Sandy limestone with *Spiroclypeus* and some rests of *Lamellibranchia.* 19x.

Fig. 7. DJAL. Recrystallized limestone with rhombohedrons of secundary calcite. 21x.

Fig. 8. SABENIBNOE. E.-island. Recrystallized limestone with *Lepidocyclina, Algae,* and rests of *Echinoidea.* 21x.

Fig. 9. SABENIBNOE. W.-island. Sandy limestone with *Spiroclypeus* and rests of *Bryozoa* and *Echinoidea.* 21x.

Fig. 10. SABENIBNOE. W.-island. Sandy limestone with a small *Lepidocyclina* and 3 big *Operculinae.* Quartz in angular grains. 21x.

Geology. — *Sur la région métallifère de Moresnet–Bleyberg–Stolberg–Limbourg néerlandais.* Par P. DE WIJKERSLOOTH. (Communicated by Prof. H. A. BROUWER.)

(Communicated at the meeting of February 27, 1937).

Dans ces dernières années plusieurs minéralisations assez importantes ont été trouvées dans la partie méridionale du Limbourg néerlandais, sur des failles de direction NO–SE à N–S. Il s'agit de systèmes de filons d'une épaisseur de 10 à 20 centimètres, qui traversent les ardoises et les grès du carbonifère. L'étude microscopique de ces minerais à la lumière réflectée a démontré qu'ils appartiennent à la même unité métallogénique que ceux de la région Moresnet–Bleyberg, de sorte que l'on doit supposer que les gîtes célèbres de celle-ci se continuent vers le Nord jusque dans la région houillère du Limbourg néerlandais. En outre la position géologique de ces minerais, notamment leur présence sur les mêmes failles qui sont minéralisées dans la région du Moresnet–Bleyberg (et du Stolberg vers l'est), démontre suffisamment la consanguinité de ces gîtes. Il n'y avait donc rien d'étonnant à ce que l'on supposât que toute la région entre le pays houiller néerlandais et le pays de Moresnet–Bleyberg (c.a.d. celle de la Gulpe et de la Geulle) pourrait être suffisamment riche en gîtes métallifères d'une certaine importance.

D'autres circonstances ont confirmé ce point de vue. On a pu conclure du caractère des minerais du houiller du Limbourg qu'ils avaient été formés à une température plus élevée que ceux de Moresnet–Bleyberg–Stolberg. Dans les minerais du Limbourg-Sud on a trouvé [1]) en effet comme substances accessoires des minéraux contenant du nickel, du cobalte, et de l'étain (le b r a v o i t e, le l i n n é i t e et le s t a n n i t e), qui sont des vrais indicateurs pour des cristallisations aux températures assez hautes.

Vu qu'autour d'un centre de minéralisation se forment des zones concentriques, qui au fur et à mesure que l'on s'éloigne de ce centre, sont caractérisées par des températures de cristallisation de moins en moins élevées („zonal arrangement of ore-deposits") il s'ensuit que les minerais

[1]) Dans la „Domaniale Mijn" à Kerkrade.

du Limbourg-Sud ont été déposés plus près du centre de minéralisation que ceux du Bleyberg et encore beaucoup plus près que ceux du Moresnet, dont les températures de cristallisation sont encore moins élevées. Cela nous fait comprendre la succession du N. au S. de zones métallifères de direction E–O. à NE.–SO, de plus en plus éloignées du foyer générateur et caractérisées chacune par les propriétés individuelles suivantes:

1°. *La zone du carbonifère du Limbourg-Sud* (températures de cristallisation élevées).
Sulfides de plomb et de zinc, bien cristallisés, qui traversent le houiller sous forme de remplissages de fractures, avec les substances accessoires: minéraux de nickel, cobalt et étain.

2°. *La zone du Bleyberg et des points méridionaux du Limbourg néerlandais* (températures de cristallisation moyennes).
Sulfides de plomb et de zinc, bien cristallisés, qui traversent les ardoises et les grès du carbonifère inférieur sous forme de remplissages de fractures, ainsi que sous forme d'amas de minerais métasomatiques dans le calcaire carbonifère à proximité du contact avec les ardoises et les grès surjacents (gîtes de contact). Dans les gîtes de cette espèce les minerais plombifères prédominent.

3°. *La zone métallifère de Schmalgraf–Moresnet–Stolberg* (températures de cristallisation basses).
Sulfides de zinc et de plomb d'une textûre microcristalline jusqu'à submicroscopique, déposés en masses écailleuses dans lesquelles le minerai de zinc domine de beaucoup le plomb, connus sous le nom de schalenblendes (Schmalgraf, Lontzen) —— ou oxydes, carbonates et silicates de zinc, notamment la calamine (Moresnet). Les deux types de minerais ont été formés dans la zone froide au dessus de la surface piézométrique, avec la seule différence que les minerais calaminaires ont été formés en présence d'un excédent d'oxygène, ce qui n'a pas eu lieu lors de la formation des schalenblendes, qui ont gardé leur caractère sulfidique.

De la répartition géographique de ces différents types il faut conclure que les solutions métalliques d'où proviennent les minerais du Limbourg-Bleyberg–Moresnet ont dévié très intensivement du Nord vers le Sud, lors de leur ascension du foyer magmatique profond, et qu'en se refroidissant ainsi progressivement elles ont déposé des gîtes de températures de moins en moins élevées, en d'autre termes, que les minerais du Moresnet–Bleyberg ont été formés par des solutions qui ont pour la plus grande part leur origine dans le sous-sol du Limbourg néerlandais et en partie de la Belgique avoisinante.

Il y a donc lieu de considérer le Limbourg néerlandais comme la région génératrice de la plus grande partie des dépôts métallifères de la Belgique limitrophe.

Pour se former une idée du chemin que ces solutions ont parcouru, il faut se rendre compte que pendant leur ascension le long des failles, elles se sont dirigées vers le Sud au contact du calcaire carbonifère perméable et des ardoises et grès imperméables sur-jacents du carbonifère.

Puisque les failles dans cette dernière série sédimentaire étaient généralement complètement bouchées (vu la grande plasticité de ces couches) les solutions métallifères n'ont pu y monter et ont dû suivre un chemin plus long à travers le calcaire carbonifère montant vers le Sud, pour apparaître au jour en territoire belge. Au contact du calcaire et des ardoises et grès du carbonifère elles ont déposé le long des failles une série d'amas lenticulaires et ordinairement irréguliers, de minerai métasomatique, caractérisé par sa richesse en plomb et cela pour la raison que le plomb se concentre de préférence en présence de la chaux. Dans les ardoises et les grès sur-jacents elles ont formé localement des filons où elles pouvaient dégager partiellement le zinc et le cuivre, vu que le zinc et le cuivre s'amassent facilement dans les grès. C'est seulement en de tels endroits, que le toit imperméable des ardoises et des grès a laissé passer en haut par exception la solution métallifère. Le plomb s'est déposé cependant plus complètement (dans le calcaire) et en plus grande quantité de sorte que les solutions métallifères en arrivant à la surface en Belgique ne contenaient principalement que du zinc. Sous l'influence de l'eau météorique, le zinc restant dans les solutions fut déposé complètement et ainsi a pu se former la riche zône zincifère du Moresnet.

La richesse du minerai de Moresnet prouve donc de son côté la richesse en substances métalliques des solutions qui, du Nord, se sont forcé un chemin le long des failles de direction NO–SE à N–S.

Par conséquent il faut admettre que la région au nord de la zone zincifère de Moresnet, parcourue par les solutions génératrices, doit être particulièrement riche en minerai et plus spécialement en minerai de plomb. Nous en trouvons la preuve dans la faille de la Geulle qui a nourri les riches dépôts plombifères du Bleyberg, situés au nord des gîtes de zinc d'Altenberg. A notre avis ce dépôt n'est qu'un seul représentant du grand nombre d'amas plombifères, situés vers le nord sur la prolongation des failles qui ont alimenté les gîtes de zinc de la région méridionale.

Si cette hypothèse est juste, il s'ensuit, que le sous-sol du Limbourg néerlandais nous offre encore des possibilités économiques inattendues.

Physiology. — *Phosphatide auto-complex coacervates as ionic systems and their relation to the protoplasmic membrane* II. By H. G. BUNGENBERG DE JONG and G. G. P. SAUBERT. (Communicated by Prof. J. VAN DER HOEVE).

(Communicated at the meeting of February 27, 1937).

INTRODUCTION.

Founded on experimental data concerning the specific properties of phosphatide coacervates, in previous Communications [1]) a conception has been formed on the structure of films which were observed on drops of these coacervates and the significance of these films for biology has been discussed. It was supposed that the phosphatide molecules are united into a double-film, as has been schematically represented in fig. 4A.

Here the positively and negatively charged ionized groups (the phosphate group and the choline and colamine groups respectively) form a suitable pattern from an electrical point of view, while the cohesion of the film is greatly promoted by appropriate non-electrolyte molecules (e.g. cholesterol). The latter, which in the mechanism of coacervation play the part of sensibilizers, were supposed to attack the lipophil parts of the phosphatide molecule, i.e. the hydrocarbon chains of the esterized fatty acids. The involved forces of affinity between the hydrocarbon chains and the sensibilizer molecules should be VAN DER WAALS forces.

Two points of these conceptions will be discussed here more in detail:

1. experiments will be discussed confirming the supposed interactions between hydrocarbon chains of fatty acids and sensibilizer molecules;
2. on the ground of recent researches it will be demonstrated in how far from the original pattern of the double-film, by means of gradual transformations, a whole series of derived double-films may be formed, which from a biological point of view are probably more important than the original.

1. *The interaction between sensibilizer molecules and hydrocarbon chains.*

If sensibilizing non-electrolytes (e.g. cholesterol) during their condensing action on phosphatide coacervates indeed attack the hydrocarbon chains of the esterized fatty acids of the phosphatide molecule, it is to be expected

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1) H. G. BUNGENBERG DE JONG and J. BONNER, Protoplasma **24**. 198 (1935) and summary in: Proc. Royal Acad. Amsterdam **38**, 797 (1935).

that an analogous condensing action will also be found in soap coacervates. We may compare the two diagrams A and B in fig. 1, where the components of the phosphatide and soap coacervates, water- and sensibilizer

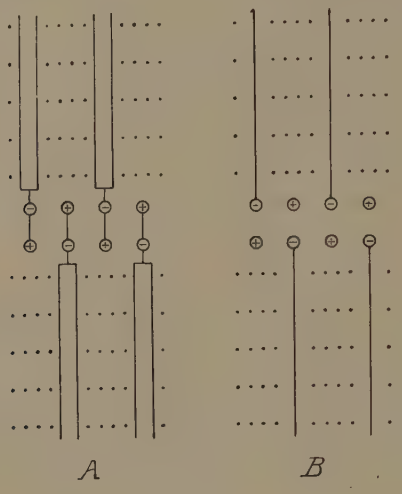

Fig. 1.

molecules being omitted, have been drawn in an ordered pattern. In the two diagrams the mutual interactions of the hydrocarbon chains have been symbolized by dotted lines. It is supposed, therefore, that in both cases the mutual cohesion of the hydrocarbon chains is strengthened by suitable sensibilizer molecules which have been put in between (represented in fig. 4 by hatched rectangles).

Starting from "amorphous" soap coacervates, i.e. coacervates in which the order of the soap molecules is still subject to strong fluctuations, gradual addition of sensibilizer molecules must then

a) *decrease* the average distance between the soap molecules in the coacervate;

b) *increase* the order of the pattern.

Consequently as a result of *a)* the coacervate will expel some of the dispersion medium, which, for example, may become apparent by separation of vacuoles; in consequence of *b)*, in case of sufficient order, the amorphous coacervate would have to give way to well oriented systems, which e.g. may be manifested by the occurrence of a double-refracting phase.

Both mentioned results are indeed found when crystals of cholesterol are brought in an amorphous coacervate of K-oleate [1]) (the liquid layer,

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[1]) Owing to the sensitiveness of these coacervates to CO_2 from the air and to relatively small oscillations of the temperature, various precautions have to be taken, which cannot be discussed here in detail. These as well as the results obtained by this method will in due time be published in Protoplasma.

rich in K-oleate, obtained by coacervation of Na-oleate solutions with concentrated KCl solutions under precisely stated conditions). It is seen under the microscope that round about the crystal in the coacervate a ring of small vacuoles occurs. On the plane of contact cholesterol/coacervate gradually double-refracting granular masses are formed with, growing out of them, strongly double-refracting myelin tubes. Cf. fig. 2.

The observed phenomena completely agree with the supposition that the sensibilizing non-electrolyte performs its function not as particles but as

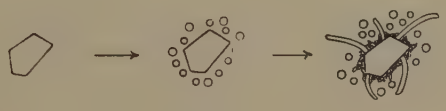

Fig. 2.

molecules. From the crystal surface cholesterol molecules are dissolved in the coacervate and there bring about condensation. The condensing action is not only limited to cholesterol but is found in numerous other non-electrolytes, such as e.g. the kindred androsteron and dehydro-androsteron. However, neither the sterine structure nor the presence of an alcohol group is required.

Even aromatic and hydroaromatic hydrocarbons have a condensing action: e.g. benzene, toluene, xylene, naphtalene, phenanthrene, cyclo-hexane, methyl cyclohexane, deca hydro-naphtalene, dihydroanthracene. [1]) In some of these hydrocarbons, however, the condensing action has not been observed by means of the qualitative method described, although it was expected: e.g. anthracene and chrysene. In all probability the dissolving-velocity is too small here.

Further analysis of the action of non-electrolytes on oleate coacervates, where we made use of quantitative methods also, led to the result that really a hydroxyl group in the molecule counteracts the condensing action. The aliphatic alcohols, for example, all have a condensing action from the fourth term onwards (n. butyl alcohol), whereas methyl, ethyl and n.-propyl alcohol effect exactly the opposite. In other homologous series (e.g. of the ketones and urethanes) it is also seen that the first terms cause the coacervate to take up liquid, whereas the higher homologues have a condensing action. All this leads to the conclusion that the condensing action starts from the hydrocarbon chains of the sensibilizer molecule and

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[1]) In case of sufficient volatility (e.g. benzene) the condensing action of the aromatic and hydroaromatic hydrocarbons as well as of many other organic compounds may likewise be proved by exposing a coacervated oleate system to their vapour. By this method it is also possible to demonstrate that the change brought about in the state of the coacervate is reversible. See for this the following Communication.

increases with the number of carbon atoms, whereas hydrophil groups weaken this action. [1])

Finally, however, there is a practical limit to this increase of the condensing action of hydrocarbons with the number of C atoms, owing to the decrease in solubility and dissolving-velocity in the aqueous surroundings. This has already been reached in anthracene and chrysene and a fortiori it is to be expected that the hydrocarbon corresponding with cholesterol is not active either. Since by our method condensation was indeed stated in case of cholesterol (as well as in androsteron and dehydroandrosteron), it seems here that by introduction of hydrophil groups sensibilization becomes possible, in spite of the fact that we have only just said that an OH group impedes sensibilization. This discrepancy is, in our opinion, merely due to the fact that the solubility and dissolving-velocity of higher aromatic and hydroaromatic hydrocarbons are too small but, on introduction of an OH group or other hydrophil groups, increase sufficiently for the condensing action to be stated by means of our qualitative method.

2. *Complex ionic systems of the type zwitterion-cation-anion.*

Some while ago we found a new type of condensed ionic systems, characterized by the fact that the complex relations (simultaneous electrostatic attraction and repulsion as the result of hydration) occur at the same time between three kinds of ions.

Thus far we had been acquainted with two types only, viz.:

A. where the complex relations are present between zwitterions mutually e.g. coacervates of iso-electric proteins), and

B. where the complex relations occur between cation and anion (complex coacervates, auto-complex coacervates and "ion-coacervates").

In the newly found type the complex relations occur between zwitterion cation and anion. As an illustration we give the following table and the

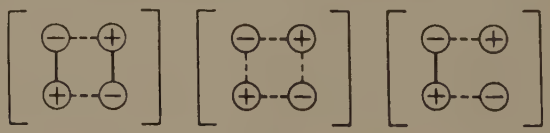

Fig. 3.

diagrams of fig. 3, while for more elaborate details the reader is referred to the original publications.[2])

We are inclined to think that the newly found type zwitterion-cation-anion may be of importance for such biological problems, for which it is a

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[1]) The extensive experimental material leading to this conclusion will in due time be published in Protoplasma.

[2]) H. G. BUNGENBERG DE JONG and G. G. P. SAUBERT, Biochem. Z. 288, 1, 13 (1936).

Table of the complex ionic systems.

Fundamental type	Examples
Zwitterion-zwitterion (fig. 3, I)	Coacervates of isolectric proteins
Cation-anion (fig. 3, II)	Complex coacervates (both ions are colloid ions). Auto-complex coacervates (one of the two ions is a colloid ion, the other a crystalloid ion). "Ion-coacervation" (both ions are crystalloid ions).
Zwitterion-cation-anion (fig. 3, III)	We know of examples where the zwitterion is a phosphatide, but also of cases where it is an isoelectric protein. The two other ions may be either both crystalloid ions or one a colloid ion, the other a crystalloid ion. Examples where both cation and anion are colloid ions are not yet known to us but in all probability they may be realized as well.

characteristic feature that a reaction or process is only accomplished when simultaneously three essential components are found together (e.g. blood coagulation and some immunological reactions).

In the following paragraph will be discussed its significance for the problem of the structure of a particular kind of films, which may be observed on phosphatide coacervates.

3. *Double-films of the type zwitterion-cation-anion.*

In the previously [1]) given representation (cf. fig. 4A), which corres-

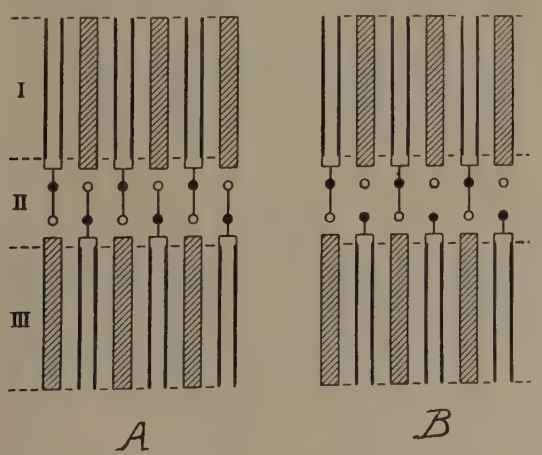

Fig. 4.

ponded with the type zwitterion-zwitterion of the complex ionic systems

1) H. G. BUNGENBERG DE JONG and J. BONNER, loc. cit.

there was the difficulty that it was not easy to conceive the condensing action of suitable bivalent cations (e.g. Ca).

Such an increase of the effective attraction of the phosphatide zwitterions might, for example, be occasioned by the fact that the originally not complete electrical compensation of the negative groups by the positive groups becomes more complete by means of special neutral salts ($CaCl_2$), when their cation ($Ca^{\cdot\cdot}$) screens off the negative charge of the phosphatide zwitterion better than their anion (Cl') does the positive charge.

However, since the materials of the film are molecules and their mutual distances can only be of molecular dimensions, it can hardly be conceived that neutral salts (e.g. $CaCl_2$, NaCl) may be taken up in this film as pairs of ions and then bring about such a screening.

In the cited publication we already said that the negative charge of the phosphatides perhaps should be ascribed only partly to the fact that in the objects examined by us not only lecithins were present but also cephalins. It was suggested that probably the negative charge is due rather to an admixture of smaller or larger amounts of acids, e.g. phosphatidic acids. However, we could not conceive how these phosphatidic acids could be taken up in the double-film of fig. 4A without breaking its continuity. Now, however, that we are acquainted with complex ionic systems of the type zwitterion-cation-anion, this participation does not meet any longer with fundamental difficulties and at the same time the regulation of the permeability by means of cations from the surroundings becomes conceivable.

If, for example, we suppose that the basic groups (e.g. choline) of the phosphatide molecules, situated in the lower half of the double-film of fig. 4A, are split off by hydrolysis and replaced by suitable cations (e.g. Ca), we have already obtained a double-film corresponding with the type zwitterion + cation + anion. Cf. fig. 4B.

From previous experiments with phosphatide coacervates we know that the maximal condensation which may be attained strongly decreases in the order $CaCl_2$ — NaCl — KCl.

If in the film of fig. 4B only Ca-ions take part, we have consequently to deal with a strongly condensed state of the film. On substitution of these by an equivalent amount of Na-ions, the permeability for water will be much more considerable, which will be the case in a still higher degree if only K-ions take part in the construction of the film.

It is besides important from a biological point of view that these double-films of the type zwitterion + cation + anion will have the character of permutoid systems.

Of the three essential kinds of participating ions two (phosphatide zwitterion and phosphatidic-acid anion) are mutually bound by great cohesion forces (VAN DER WAALS forces between the hydrocarbon chains mutually and between these and sensibilizer molecules respectively), the third, however, the cation, is not and consequently will be proportionally

easily interchangeable with other cations from the surroundings. A double-film, containing only Ca-ions, brought into contact with a NaCl solution, will replace Ca-ions by Na-ions till a certain ratio Ca/Na has been formed in the surroundings, which as an equilibrial concentration belongs to the partially permuted double-film.

Conversely, a double-film which only contains Na-ions, brought in a $CaCl_2$ solution, will replace Na-ions by Ca-ions, again until an equilibrium has been formed between film and solution. It will be clear that in the former case the permeability for water will have increased, in the latter case decreased.

Since the affinity of the Ca-ions to the negative phosphate group is far greater [1]) than that of the Na-ions, in mixtures of $CaCl_2$ and NaCl the ratio Ca : Na will always have to be considerably greater in the film than in the salt solution which is in equilibrium with it. That means that already a relatively small quantity of Ca added to a given NaCl solution may result in a considerable substitution of Na-ions in the film by Ca-ions, accompanied by a decrease of the permeability for water.

Consequently, owing to the character of the double-films considered here as permutoid systems, we do not find here the fundamental difficulty existing, with regard to the regulation of the permeability by neutral salts, for double-films which are built up only of zwitterions.

For the rest it stands to reason that double-films of the type zwitterion + cation + anion need not be limited to the given example. On the one hand it is possible that biological films may be realized which, as regards their structure, may be considered as intermediate cases between A and B of fig. 4. On the other hand double-films are conceivable in which, instead of the phosphatidic-acid anion, another suitable anion participates, e.g. a protein-colloid anion. It is particularly the latter combination which may be important from a biological point of view, since also in discussions on the nature of the protoplasmic membrane the possibility is considered whether this cannot consist of protein + phosphatide.

Leiden, January 1937.

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[1]) As a measure for the affinity of cations to the phosphate group the concentration at the reversal of charge may be used; viz. the affinity is larger as this concentration is smaller. The concentration of $CaCl_2$ at the reversal of charge depends on origin and degree of purity of the phosphatide preparation but usually lies between 1—100 m. equiv., that of NaCl lies always in the order of 2—2.5N, while that of KCl lies still higher and in a solution saturated with KCl usually is not even reached.

Physiology. — *Models for the stimulation of the organ of smell.* By H. G. BUNGENBERG DE JONG and G. G. P. SAUBERT. (Communicated by Prof. J. VAN DER HOEVE).

(Communicated at the meeting of February 27, 1937).

However complex may be the whole series of succeeding events which ultimately lead to the sensation of smell, it is obvious that as a first link the molecules of the smelling substance penetrate from the gas-phase into a certain substrate of the cells of the organ of smell and in this substrate cause a fundamentally reversible change in condition.

It may further be considered likely that this change in condition is accompanied by a change in permeability. On the ground of generally physiological considerations it may then be expected that phosphatides will to a large extent take part in this substrate. Our own experience concerning the colloid chemistry of the phosphatides strongly supports this suggestion. Colloid systems, e.g. sols or coacervates of proteins, substances with the nature of carbohydrates, nucleinates, etc., are as a rule comparatively insensitive to the majority of the organic non-electrolytes. They do show changes in condition with a limited number, e.g. alcohol, acetone, etc., but only in relatively very high concentrations, while some are sensitive to phenols in considerably smaller concentrations.

On the other hand sols and coacervates of phosphatides are highly sensitive to the most divergent types of compounds in organic chemistry and this influence is often already perceptible in relatively very small concentrations [1]). This striking difference with the behaviour of the proteins, etc. is due to the fact that the phosphatides are not only hydrophil but also, owing to the presence of long hydrocarbon chains in the molecule, to a marked degree lipophil [2]).

As we have recently found, with regard to this sensitiveness to numerous organic non-electrolytes, colloid oleate systems are closely connected with the phosphatides [3]).

This is not surprising, since, though greatly differing in molecular structure, phosphatides and oleates have in common the long, partially unsaturated, hydrocarbon chains.

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[1]) H. G. BUNGENBERG DE JONG and R. F. WESTERKAMP, Biochem. Ztschr. **248**, 335 (1932).

[2]) H. G. BUNGENBERG DE JONG and J. BONNER, Protoplasma **24**, 198 (1935) and Summary in Proc. Royal Acad. Amsterdam **38**, 797 (1935).

[3]) A detailed publication will in due time be made in Protoplasma. Some of the obtained results as well as their interpretation have already been mentioned in the immediately preceding Communication.

With regard to what was suggested above concerning the first link in forming the stimulus of smell, it is interesting that coacervates both of phosphatides and oleates appear to be sensitive to the vapour of numerous organic non-electrolytes. The molecules which are transported by the gas-phase and have entered into the coacervate occasion changes in condition which are reversible and appear to be a decrease or increase of the average distance of the phosphatide and oleate molecules respectively in the coacervate.

Without entering into details, one of the morphological criteria for this decrease or increase may be mentioned here. We refer here to the vacuolization phenomena which on supply or eduction of the organic vapour may be perceived with the microscope on coacervate drops which are suspended in their equilibrial liquid.

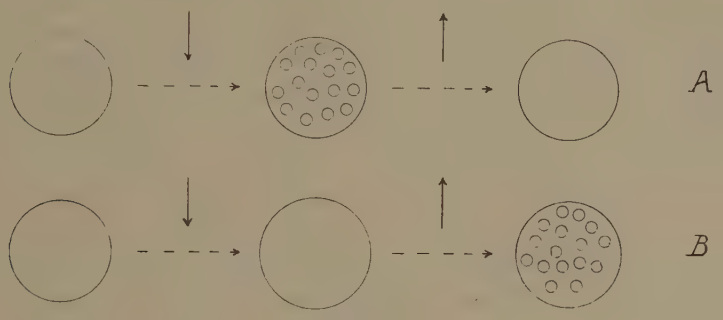

Fig. 1.

1st case (fig. 1A).

If on supply of the vapour (represented by ↓) vacuolization sets in, which after eduction of the vapour (represented by ↑) disappears again, it means that the organic non-electrolyte causes condensation of the coacervate: Under the influence of the introduced organic molecules, the phosphatide and oleate molecules respectively come to be situated at a smaller average distance from each other, while they separate a liquid, containing only a small amount of phosphatides or soap, in vacuolar form. Example for oleate coacervates: nitrobenzene.

2nd case (fig. 1B).

If vacuolization is observed, not on supply of the vapour, but after it has acted for some time and then is carried off, we may conclude to the reverse. Under the influence of the organic non-electrolyte the coacervate now slowly or quickly takes up liquid from the surroundings, which on eduction of the vapour separates again in the coacervate drop in vacuolar form. Example for oleate coacervates: paraldehyde.

In a certain sense and with some reserve these coacervates, which are sensitive to the vapours of organic substances, may be considered as models for the physiological substrate on which the smelling substance primarily acts. For not only are these coacervates sensitive to practically all suffi-

ciently volatile substances and is the change in condition which was brought about reversible, but also the nature of this change in condition (decrease and increase respectively of the average distance between the essential highly molecular components: phosphatide and oleate molecules respectively) is such that in analogous systems containing far less water it would have to manifest itself as a change in permeability (for water, possibly anorganic ions).

It is further interesting that the action of an organic substance, according to its nature, may become manifest in one of two opposite qualities. This reminds us somehow of the principal classification, given by ZWAARDEMAKER [1]), of the odours into two groups: "odeurs nutritives" and "odeurs de décomposition".

Here is also offered a simple explanation of the remarkable fact that two smelling substances in exactly tuned concentrations in the air may lead to the disappearance of the sensation of smell.

However, our model offers still more points of contact with the physiology of smell. By the side of the above-mentioned two cases we know yet a third:

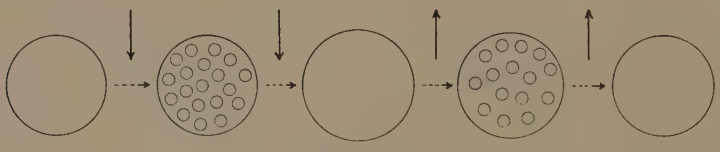

Fig. 2.

3rd case (fig. 2).

On supply of the vapour a temporary vacuolization sets in; similarly on eduction of the vapour (e.g. amylene hydrate in case of oleate coacervates). This means consequently that a small amount of the penetrated organic substance has a condensing action but a large quantity again enlarges the mutual distance of the oleate and phosphatide molecules respectively.

We are inclined to look for a connection here with the fact that certain smelling substances at a small concentration in the air give a pleasant sensation, at a higher concentration, however, an unpleasant one.

With a view to the physiology of smell the following results of a more elaborate research (partially obtained with other, also quantitative methods) are also worth mentioning.

1. In a homologous series each following term is already active at smaller concentrations than the preceding one.
2. The quality of the action may be reversed in some homologous series (e.g. alcohols, ketones, etc.).

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[1]) H. ZWAARDEMAKER, l'Odorat, Encyclopédie Scientifique publiée sous la direction du Dr. TOULOUSE, Gaston Doin, Paris 1925, p. 219.

For the normal alcohols in the case of oleate coacervates this reversal lies at the 4th term (for methyl, ethyl and n. propyl alcohol see fig. 1*B*, for n. butyl alcohol and higher homologues on the other hand see fig. 1*A*) [1]).

Ad 1. It may yet be remarked that even a highly molecular and practically non-volatile alcohol as cholesterol, brought into direct contact with an oleate coacervate, still causes condensation, not however, when the coacervated system is separated from the cholesterol crystals by the gas-phase.

In model experiments for the stimulus of the organ of smell consequently natural limits to the rule mentioned under 1) are formed by the decreasing vapour tension and insufficient solubility in the aqueous surroundings in which the coacervate drops are suspended. In the physiology of smell also an analogue is found, where the rule applies that substances with a boiling-point higher than about 300° do not give a sensation of smell.

Ad 2. The observed change in quality of the action on the coacervate somewhat reminds us of the change in quality of the odour in homologous series, although there the latter does not occur by leaps and bounds but gradually.

In order to reduce the range of the discussed model to its correct proportion, the poverty in possibilities of reaction, in connection with the great variety of odours, has to be taken into consideration. Attempts to interpret all the familiar data of the physiology of smell by the changes in condition of only one and the same substrate which is used in the model, must consequently fail in many respects. This is indeed the case, as may appear from *A*) and *B*) below.

A) The classification into „odeurs nutritives" and „odeurs de décomposition" does not coincide with each time one of the two possibilities of reaction (figs 1*A* and *B*) of the oleate coacervate. In either group substances are found enlarging the average distance between the oleate molecules in the coacervate as well as substances which bring about the reverse.

B) In the physiology of smell indeed transitions in quality of the odour are found in homologous series, but these seem to be limited to each of the mentioned principal groups, while transitions between „odours nutritives" and „odeurs de décomposition" do not seem to occur there. If in our model we should try to connect each of these principal groups with the two possibilities of reaction *A* and *B* of fig. 1, this model, as appears from 2.), in homologous series indeed exhibits transitions between these two principal groups.

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[1]) In the immediately preceding Communication this reversal of the action has already been briefly discussed and explained.

Summarizing, we may therefore say that our model indeed contains a fairly large number of elements which each give occasion to interesting analogies with the physiology of smell but that these elements are not mutually coordinated in the right way.

For an interpretation of the data of the physiology of smell on this basis it is inevitable that we do not confine ourselves to one single model for the substrate of smell but consider the cooperation of a whole series of these models with sensitivities which each time are again differently tuned.

Similarly in the physiology of smell for each of the 9 classes of odours at least specially tuned cells of the organ of sense had to be assumed, which, according to ZWAARDEMAKER, should even be spread sterically in 9 areas of the organ of smell.

With regard to a study of analogous models, where the sensitive substrate contains other essential kinds of molecules, we have only just started. They have already shown that here the classification of the volatile substances into two principal groups, according as their action causes the coacervate to contain more or less liquid, may turn out differently from that of the oleate coacervate.

By the side of this it is interesting that already another physical-chemical condition of the substrate, although the essential kind of molecules present in it is the same, can lead to this as well. We refer here to anisotropic oleate and phosphatide systems, which likewise are sensitive to a great number of organic vapours.

Benzene, for example, which has a strongly condensing effect on amorphous oleate coacervates (fig. 1*A*), occasions exactly the opposite in certain anisotropic oleate systems (Under liquid uptake from the surroundings the double refraction disappears). Just as in amorphous oleate coacervates, the change brought about in the condition of these anisotropic systems, on eduction of the vapour, is reversible: (the double refraction returns).

From all this it may appear that the models discussed here for the stimulation of the organ of smell are as yet in their initial stage and that only after a more elaborate research a more fertile comparison with the data of the physiology of smell will be possible.

Leiden, January 1937.

Neurology. — *Ueber eine direkte Verbindung von der Kleinhirnrinde nach dem Nucleus Deiters.* Von SVEN BERGGREN. (Aus dem Laboratorium der psychiatrisch-neurologischen Klinik, Utrecht.) (Communicated by Prof. C. WINKLER.)

(Communicated at the meeting of February 27, 1937).

Dem Nucleus Deiters, der als einer der wichtigsten Reflexzentren des Vestibularissystems angesehen wird, werden vor allem aus dem Nervus vestibularis und dessen sekundären Kernen und aus den medialen Kleinhirnkernen durch den Tractus uncinatus Fasern zugeführt.

Wenn man bei einem Normalpräparat von der Gegend ausgeht, wo das Corpus restiforme dorsalwärts umschlägt um in das Kleinhirn einzustrahlen, findet man die grossen Zellen des Nucleus Deiters an seiner Medialseite gelegen und darunter quergeschnittene Fasern. Diese Fasern bilden das sog. Corpus juxtarestiforme, das aus dem Nucleus triangularis N. VIII entsteht und mit dem Corpus restiforme nach dem Kleinhirn umschlägt um nach Durchbohrung des Anfanges des Bracchium conjunctivum als die sog. Fibrae perforantes in den medialen Kleinhirnkernen zu enden. Wenn man aber diese Einstrahlung der Fibrae perforantes in die Kleinhirnkerne näher betrachtet, scheint es, als ob einzelne der Fasern durch oder zwischen den Kernen nach der Kleinhirnrinde verfolgt werden könnten. Teilweise mag es sich bei diesem scheinbaren Durchbohren von Fasern nur um ein Begegnen von Fasern der Fibrae perforantes und Fasern aus der Kleinhirnrinde, die ebenfalls in den Kernen enden, handeln. Aus dem anatomischen Bild darf man aber vermuten, dass es unter den Fibrae perforantes auch ev. direkte Fasern zwischen der Kleinhirnrinde und den vestibulären Kerngebieten gäbe. Aus der Literatur ergibt sich auch, dass solche direkte Fasern, und zwar Neuriten der Purkinjeschen Zellen nach dem Nucleus Deiters, von LORENTE DE Nó beschrieben worden sind. Als Ursprungsgebiet dieser Fasern, die mittels der Cajalschen Silberimprägnationsmethode gefunden wurden, wird der Flocculus, der Lobus medianus und der Lobus paramedianus angegeben. Aus den letzteren Gebieten sollten sie gekreuzt verlaufen.

Im Nachfolgenden mögen einige Marchipräparierte Kaninchengehirne beschrieben werden, welche eine Beschädigung der Rinde des Kleinhirns zeigten, und zur Beleuchtung dieser Fragen sehr geeignet waren. Die Serien sind aus dem Laboratorium von Prof. WINKLER und waren für andere Zwecke hergestellt, nämlich um die Marchidegeneration nach Mittelhirnläsionen zu studieren.

In drei von fünf Fällen ist die Läsion der Kleinhirnrinde eine ganz

oberflächliche und begrenzt auf dem Sulcus paramedianus und die unmittelbar angrenzenden Teile des Vermis und des Lobus paramedianus. Die Läsion geht kranialwärts nicht an der Fissura primaria vorbei und auch der Pars floccularis ist unbeschädigt. In diesen drei Fällen findet

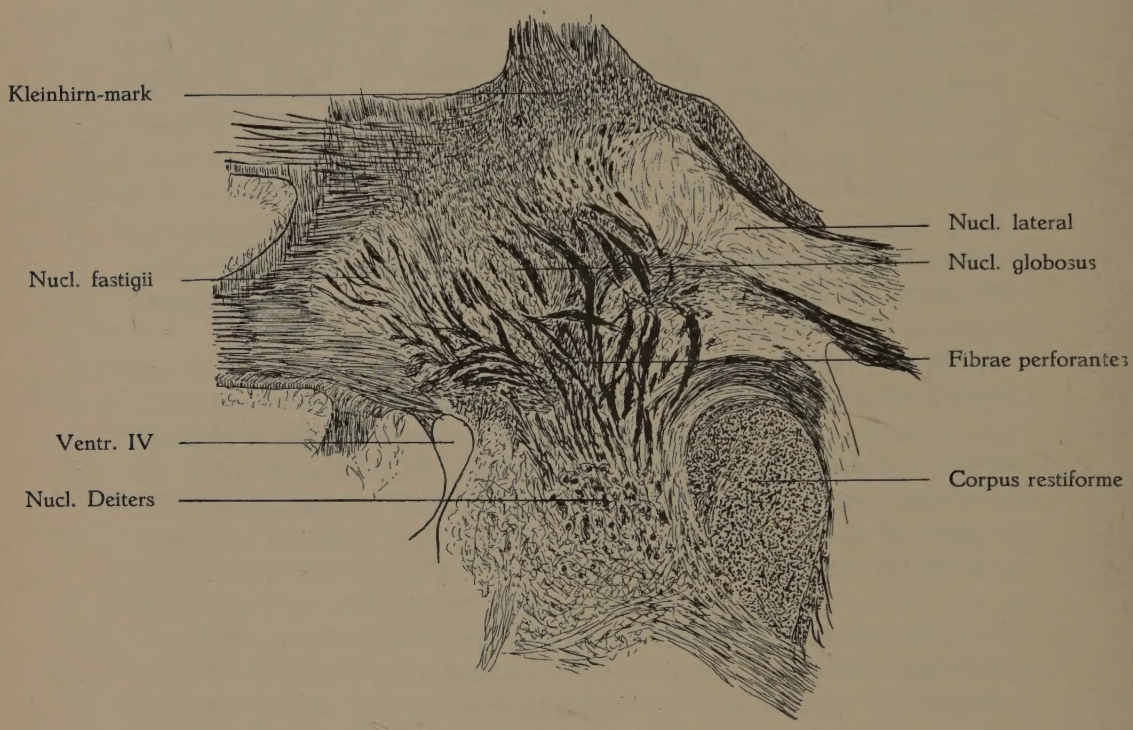

Abb. 1. Normalserie von Kaninchen. Präp. nach WEIGERT—PAL. Transversalschnitt durch verlängertes Mark und Kleinhirn in der Gegend des Nucleus Deiters. Die Fibrae perforantes treten als deutliche Bündel hervor.

man im Mark eine ausgiebige Degeneration, die sich von der Gegend der Läsion nach den centralen Kernen ausbreitet, und zwar ganz vorwiegend nach derselben Seite. Die Degeneration verliert sich grösstenteils in diesen Kernen, aber viele degenerierte Fasern setzen sich in den oben beschriebenen Fibrae perforantes fort und können darin deutlich nach dem Nucleus Deiters verfolgt werden, in dessen dorsalem Teil sie enden (Abb. 2). Unter den Fibrae perforantes der entgegengesetzten Seite konnten nur sehr spärliche degenerierte Fasern gefunden werden.

In den zwei anderen Fällen war die Läsion innerhalb des Vermis tiefer und reichte bis an die dorsokaudale Begrenzung der Nuclei fastigii. Die Degeneration im Mark verliert sich auch hier zum grössten Teil in den Kernen, aber setzt sich wie in den vorigen Fällen auch unter den Fibrae perforantes und zwar doppelseitig nach dem Nucleus Deiters fort. Eine Beschädigung der Kerne kann in diesen zwei Fällen nicht ausgeschlossen werden. Da aber zwischen diesen und dem Nucleus Deiters keine andere

Verbindung als der Tractus uncinatus bekannt ist, darf man wohl annehmen, dass es sich hier um direkte Rindenfasern handelt. Die Doppel-

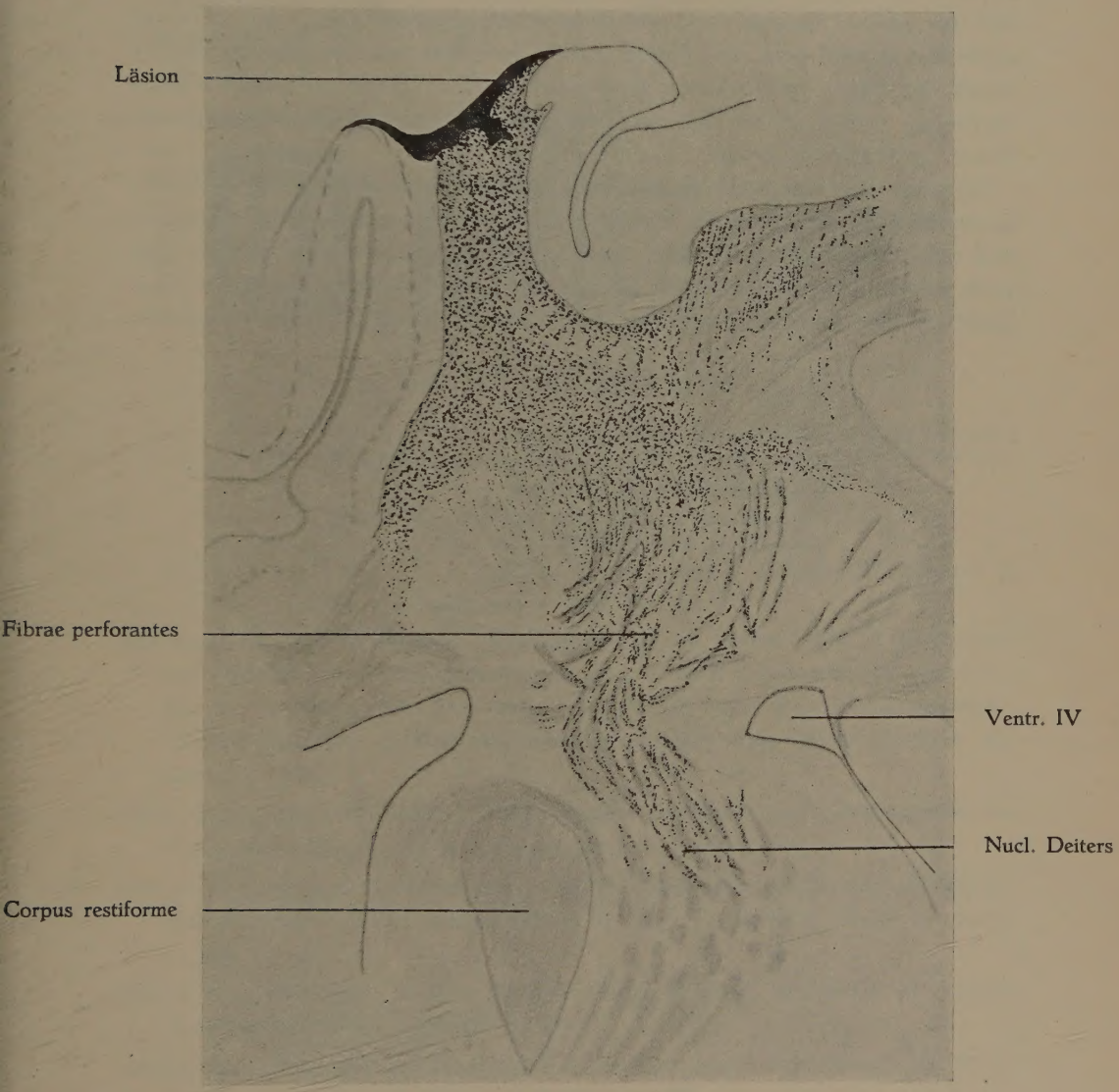

Abb. 2. Transversalschnitt an derselben Stelle als Abb. 1. eines Kaninchengehirnes, wo eine oberflächliche Läsion um der Sulcus paramedianus vorhanden war. Die sekundäre Degeneration verliert sich grösstenteils in den Kleinhirnkernen, aber viele Fasern setzen sich als Fibrae perforantes nach dem Nucleus Deiters fort.

seitigkeit und auch das reichlichere Vorkommen im Vergleich mit den anderen drei Fällen lässt sich aus der Tiefe und der symmetrischen Lage der Läsion erklären.

Dass die beschriebene Verbindung ganz überwiegend eine ungekreuzte

ist, geht besonders deutlich aus einer Serie hervor, in welcher das Kleinhirn in der Sagittalebenen gespalten wurde. Neben dem Sagittalschnitt war die Rinde in der Umgebung des linken Sulcus paramedianus beschädigt. Neben der für diese Operation karakteristischen Degeneration des Tractus uncinatus konnte man eine Degeneration von dem beschädigten Rindenteil durch die Fibrae perforantes nach dem Nucleus Deiters derselben Seite verfolgen, während an der anderen Seite nur vereinzelte degenerierte Fasern gefunden wurden.

Es muss also eine nicht zu spärliche direkte Verbindung von der Kleinhirnrinde nach dem Nucleus Deiters beim Kaninchen angenommen werden, und diese Verbindung ist ganz vorwiegend eine ungekreuzte. Ob es aber auch andere Ursprungsgebiete als die oben beschriebenen für diese Verbindung gibt, lässt sich aus dem vorliegenden Material nicht schliessen.

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